

Effect of Pd Coordination and Isolation on the Catalytic Reduction of O₂ to H₂O₂ over PdAu Bimetallic Nanoparticles

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KEYWORDS: *Single atom alloys, hydrogen peroxide synthesis, oxygen reduction, geometric effects, DFT, FTIR, EXAFS.*

ABSTRACT: The direct synthesis of hydrogen peroxide ($\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2$) may enable low-cost H_2O_2 production and reduce environmental impacts of chemical oxidations. Here, we synthesize a series of PdAu_x nanoparticles (where $0 \leq x \leq 220$, ~ 10 nm) and show that, in pure water solvent, H_2O_2 selectivity increases with the Au to Pd ratio and approach 100% for Pd₁Au₂₂₀. Analysis of *in situ* XAS and *ex situ* FTIR of adsorbed ¹²CO and ¹³CO show that materials with Au to Pd ratios of ~ 40 and greater expose only monomeric Pd species during catalysis and that the average distance between Pd monomers increases with further dilution. *Ab initio* quantum chemical simulations and experimental rate measurements indicate that both H_2O_2 and H_2O form by reduction of a common OOH*-intermediate by proton-electron transfer (PET) steps mediated by water molecules over Pd and PdAu_x nanoparticles. Measured apparent activation enthalpies and calculated activation barriers for H_2O_2 and H_2O formation both increase as Pd is diluted by Au, even beyond the complete loss of Pd-Pd coordination. These effects impact H_2O formation more significantly, indicating preferential destabilization of transition states that cleave O-O bonds reflected by increasing H_2O_2 selectivities (19 % on Pd; 95 % on PdAu₂₂₀) but with only a three-fold reduction in H_2O_2 formation rates. The data imply that the transition states for H_2O_2 and H_2O formation pathways differ in their coordination to the metal surface, and such differences in site requirements require that we consider second coordination shells during design of bimetallic catalysts.

1. Introduction

Catalysts consisting of alloyed nanoparticles often provide higher rates or selectivities for desired reactions than respective pure metal catalysts.¹⁻⁴ Particularly significant examples of industrially relevant alloyed catalysts include PdAg^{5,6} and PdPb⁷ for alkyne semihydrogenation, PtSn for alkane dehydrogenation,⁸ PdAu for vinyl acetate monomer synthesis,⁹ and PtRh for simultaneous NO_x reduction and CO and hydrocarbon oxidation.¹⁰ Differences in catalytic reactivity between monometallic and alloyed nanoparticles are frequently attributed to changes in the electronic structure caused by formation of heteronuclear metallic bonds or differences in the number and identity of reactive metal atoms present in ensembles that form active sites for catalysis. These phenomena are denoted as electronic and geometric effects, respectively.^{2, 11-13} In addition, surfaces of alloy nanoparticles expose multiple metallic elements that will possess distinct binding energies for reactive species, and the resultant changes in the coverage of catalytic intermediates may influence reaction rates.¹⁴ Differences in binding ener-

gies for adsorbates between the constitutive metals in an alloy can also cause the surface structures to change in response to the chemical environment. For example, oxygen binds more strongly to Pd than Au, and therefore, oxidative treatments tend to enrich surfaces of PdAu materials with Pd atoms in comparison to surface in inert environments or vacuum.¹⁵⁻¹⁷

Electronic effects of alloying on catalysis largely stem from changes in the *d*-band structure of metal surfaces due to, *inter alia*, orbital rehybridization, charge transfer and tensile strain.^{1, 2, 13} The geometric effects of alloy formation in surface chemistry arise when the inclusion of a second element disrupts monometallic ensembles of contiguous metal atoms, which alters the stability of adsorbed intermediates. Multidentate organic adsorbates and reactive intermediates strongly sense these differences because charge transfer *via* M-O and M-C bonds between the surface and adsorbates depend upon the elemental identity of the metal.¹⁸ The adsorption of CO on Pd and PdAu surfaces provides archetypal examples: Pd predominantly binds CO at two-fold

bridge (μ^2 -CO) and three-fold hollow sites (μ^3 -CO), however, the disturbance of these ensembles drives CO to bind preferentially at atop sites (η^1 -CO) comprised of Pd atoms within PdAu alloys.¹⁹

PdAu alloys provide catalytic rates and selectivities that exceed those of monometallic Pd or Au catalysts, however, ascertaining the reasons for these differences remains a challenge. The formation of PdAu alloys modifies both the electronic and geometric structure of Pd, which has been demonstrated by investigations that involve X-ray photoelectron spectroscopy (XPS),²⁰⁻²² X-ray absorption spectroscopy (XAS),^{20, 22-37} and Fourier transform infrared spectroscopy (FTIR) of adsorbed CO.^{9, 19, 25, 28, 30, 32, 33, 37-46} These two effects are entangled and complicate the interpretation of data obtained by these methods, because the atomic composition and arrangement of PdAu alloy surfaces affects the electronic structure. Pd and Au are miscible and form a substitutional, exothermic alloy ($-2 > \Delta H_{mix} > -9$ kJ mol⁻¹) for all compositions.⁴⁷⁻⁴⁹ As such, Monte Carlo simulations of PdAu materials predict the formation of significant numbers of isolated Pd monomers when the mole fraction of Au greatly exceeds that of Pd.⁵⁰⁻⁵² Most results indicate that Pd atoms gain *d*-electrons as the Au contents in PdAu alloys increase. This conclusion agrees with clear evidence from *ex situ* XANES spectra that reveal a less intense whiteness at the Pd L₃ edge for Pd₁Au₁ nanoparticles compared to monometallic Pd.²² Hence, numerous spectroscopic and computational investigation indicate that alloying Pd with Au modifies the electronic structure of Pd atoms in manners that seem relevant for catalysis.

In the limit of high Au to Pd ratios (e.g., Pd₁Au₂₂₀), Pd atoms at the surface of nanoparticles exist primarily as monomers, and these materials are denoted as PdAu single-atom alloy (SAA) catalysts.⁴ SAA nanoparticles of PdAu or other combinations of elements exhibit emergent electronic and geometric properties described in recent publications.^{4, 53} Valence band XPS spectra of Cu single-atoms in Ag⁵⁴ and DFT calculations of electronic structure for a library of Pt, Pd, Ir, Rh and Ni single atoms in Au, Ag and Cu consistently show narrow *d*-bands in SAAs relative to pure metal caused by poor orbital hybridization due to a lack of homonuclear bonding materials.⁵³ These narrow *d*-bands generally give rise to greater extents of charge transfer between metal surfaces and monodentate adsorbates and more exothermic adsorption.⁵⁴ Consequently, these changes provide an opportunity to selectively destabilize multidentate surface intermediates relative to monodentate species, and thereby, significantly change rates and selectivities for catalytic reactions. Moreover, the formation of isolated active sites may reduce the translation entropy of adsorbates.⁵⁵ Recent experimental studies show that PdAu SAAs give greater rates and selectivities than monometallic Pd or Au nanoparticles for alcohol oxidation,³⁴ vinyl acetate synthesis,⁹ Ullmann coupling,⁴⁴ and selective hydrogenations of alkenes and alkynes.^{40, 43}

PdAu alloys also form H₂O₂ more selectively during the direct synthesis reaction ($H_2 + O_2 \rightarrow H_2O_2$) than monometallic Pd and with much greater rates than Au.^{56, 57} All known catalysts for direct synthesis form H₂O₂ by sequential oxygen reduction steps and produce water following irreversible O-

O bond rupture in chemisorbed dioxygen (O₂*), hydroperoxide (OOH*), or hydrogen peroxide (H₂O₂*), such that O-O cleavage events always reduce H₂O₂ selectivities and yields.⁵⁸ Common strategies to suppress O-O bond rupture and increase H₂O₂ selectivities involve the addition of promoters such as CO₂,^{56, 57} acids,^{59, 60} and halide ions like Br^{-61, 62} and Cl⁻⁵⁹. Despite their frequent use, liquid-phase acid and halide promoters present drawbacks that include catalyst deactivation by metal dissolution (leaching),⁶² the need for corrosion resistant reactors, and challenges in purifying the product for downstream processes. An alternative strategy involves alloying the active metal (typically Pd or Pt) with another, ostensibly inert, metal to form bimetallic catalysts (e.g., PdAu,^{39, 41, 45, 56, 57, 62-64} PtAg,⁶⁵ PdZn,^{60, 66} PdIn,^{60, 66, 67} PdGa,^{60, 66, 67} PdSn,^{60, 66} PdTe,⁶⁸ and PdSb⁶⁹). Among these bimetallic catalysts, PdAu has received the most attention.

Despite numerous investigations that report the production of H₂O₂ over PdAu nanoparticle catalysts, the molecular and kinetic basis for the increases in H₂O₂ selectivity and the quantitative relationship between rates and catalyst metal content remain controversial. Investigations consistently show that the addition of Au to Pd nanoparticles increases H₂O₂ selectivities. A fraction of the prior studies find that H₂O₂ formation rates and selectivities reach maximum values at mean atomic ratios of Pd to Au near two,^{39, 45, 62, 63, 70-72} however, the remainder suggest that selectivities increase monotonically with the ratio of Au to Pd.^{41, 45, 57}

Different explanations for the method by which Au confers greater H₂O₂ selectivities to PdAu catalysts accompany each of these varied observations. First, differences in selectivities may arise from charge transfer between Au and Pd, which results in changes to the electronic structure of the exposed Pd atoms. This interpretation seems consistent with a recent study from our group that shows activation enthalpies for both H₂O₂ and H₂O formation increasing from -3 to 17 kJ mol⁻¹ and 11 to 32 kJ mol⁻¹, respectively, across a series of catalysts with metal contents varying between monometallic Pd and Pd₁Au₁₃, which correlates with an increase in H₂O₂ selectivity from 23% to 60%.⁴¹ These considerations agree also with the proposal that Au increases H₂O₂ selectivity by increasing the oxidation state of Pd based upon comparisons of kinetic data to *ex situ* XPS measurements of untreated Pd and PdAu materials,⁷³ yet contradicts findings from DFT and XANES (*vide supra*). Experimental studies typically utilize chloride precursors for Au, which leave detectable levels of Cl-species that tend to oxidize metal atoms and impact reactivity.^{61, 73} Second, comparisons between *in situ* X-ray absorption spectroscopy (XAS) and rate and selectivity measurements have been taken as evidence that the greater H₂O₂ selectivity of PdAu catalysts results from the suppression of a Pd hydride phase, which has been proposed to be less selective to H₂O₂ formation than metallic Pd.^{64, 74} Rate measurements performed at low conversion and with *in situ* XAS⁷⁵ show that 9 nm nanoparticles of Pd atoms give much greater H₂O₂ selectivities when these exist as β -PdH_x (55% to H₂O₂) compared to when these same nanoparticles reside in a metallic state (22% to H₂O₂) nanoparticles. Third, critical reviews of literature suggest that the dilution of Pd by Au may be responsible for the increases in selectivity^{49, 76} but little direct experimental evidence supports this hypothesis or describes if the origin of

these changes are electronic or geometric effects. Fourth, and finally, the addition of Au and the changes in surface composition may alter the mechanisms for H₂O₂ or H₂O formation or the identities of the most abundant reactive intermediate present at common conditions as electrochemical oxygen reduction reaction pathways may change with catalyst or applied potential.^{77, 78} Few studies have tested all of these hypotheses, and none have examined the possibility that reasons for the rise in H₂O₂ selectivity may change along with the Au to Pd ratio and prevailing surface motifs.

Here, we determine how Au increases selectivities for H₂O₂ formation by comparing results from steady-state measurements of H₂O₂ and H₂O formation rates on a series of highly uniform Pd₁Au_x nanoparticle ($x = 0, 3, 18, 37, 50, 220$) catalysts, detailed characterization of the structure of these nanoparticles obtained from *in situ* XAS and *ex situ* FTIR of adsorbed CO, and *ab initio* calculations of plausible reaction pathways on representative model surfaces. These findings show that the elementary steps and intermediates for these reactions remain constant for Pd and all PdAu_x materials despite large differences in rate, selectivities and apparent barriers for H₂O₂ and H₂O formation. These changes clearly correlate with reductions in the Pd-Pd coordination number, and at higher Au to Pd ratios, the distance between Pd monomers. Experimental measurements and DFT results agree quantitatively and demonstrate that differences between activation enthalpies for the formation of H₂O₂ and H₂O increase with the ratio of Au to Pd on nanoparticle surfaces. Those enthalpic barriers for H₂O formation increase by ~ 60 kJ mol⁻¹ across this series of materials, however barriers for H₂O₂ formation change by only 20 kJ mol⁻¹. The differences among these barriers lead the H₂O₂ selectivities that approach 100% for the greatest Au to Pd ratios. The *d*-band structure of Pd evolves with the dilution of Pd in the PdAu(111) surfaces, which prevents complete deconvolution of electronic and ensemble effects. While the *d*-band structure of Pd(111) differs significantly from all PdAu_x(111) surfaces examined, the differences among the densities of states upon Pd for the PdAu_x(111) models are comparatively small and imply that selectivity improvements depend most directly on changes in geometric structure despite the necessary covariance of electronic and geometric structures. These comparisons provide compelling evidence that the increased selectivities for H₂O₂ reflect the differences between the active site requirements (i.e., ensemble size) for the transition states that form H₂O₂ and H₂O, which identifies the isolation of monomeric active sites as a catalyst design strategy to increase H₂O₂ selectivity.

2. Materials and Methods

2.1. Synthesis of SiO₂ Supported Au Nanoparticles

Silica (Sigma-Aldrich, Davisil 646, 35-60 mesh) was used as received. Au nanoparticles were deposited by a method that involved strong electrostatic adsorption of Au ethylenediamine complexes that form spontaneously following the combination of HAuCl₄ (Sigma-Aldrich, >49 wt% Au) and ethylene diamine (Sigma-Aldrich, >99%) in deionized (DI) water (>17.8 MΩ cm resistivity). Au-SiO₂ (2.0 wt %)

was prepared by dissolving HAuCl₄ (1.6 g) and ethylenediamine (5 cm³) into DI water (100 cm³) with the intent to exchange Cl⁻ ligands on Au for ethylenediamine ligands.^{19, 33, 79-82} A dark brown precipitate forms following the addition of ethylenediamine, however, the precipitate dissolves with stirring at ambient temperature and yields a clear orange solution. In a separate beaker, silica (40 g) was added to a solution of deionized water (600 cm³) and concentrated NH₄OH (100 cm³; Macron, 28-30% NH₄OH). The clear solution containing gold-ethylenediamine complexes was added to the basic solution containing SiO₂, and the resulting mixture was stirred continuously with a plastic spatula for 10 minutes, followed by intermittent stirring every 10 minutes for 1 h to provide time for cationic Au-ethylenediamine complexes to adsorb to anionic moieties on the silica surface. The solids were filtered, washed with DI water (40 cm³ g⁻¹) and vacuum filtered to recover the damp solids. These solids were heated in a flowing (200 cm³ min⁻¹) mixture of H₂ (20 kPa; Airgas, UHP) and He (81 kPa; Airgas, UHP) to 413 K at 3 K min⁻¹ in a tube furnace and held at 413 K for 90 min with the intent to evaporate water and reduce the Au-complexes to form uniform Au nanoparticles on silica. Samples containing different amounts of Au on silica were prepared by analogous procedures in which the ratio of HAuCl₄ to ethylenediamine and the volume of the basic solution remained constant, but the quantity of Au and silica were changed to achieve the desired Au content.

2.2. Electroless Deposition of Pd onto Supported Au Nanoparticles

Pd was selectively deposited onto the existing Au nanoparticles by electroless deposition from aqueous Pd(NO₃)₂ (Sigma-Aldrich, $\sim 40\%$ Pd) in an ice bath (~ 273 K).^{66, 83, 84} In a typical synthesis, Au-SiO₂ (5 g) was soaked for 10 minutes with DI water (150 cm³) and decanted five times to remove a yellow leachate. The washed solids were transferred to a spinner flask with a suspended magnetic stir bar (used to minimize attrition of the silica particles), placed in an ice bath, and then allowed to cool for 30 minutes. Subsequently, an aqueous solution of Pd(NO₃)₂ (≤ 0.2 mM Pd(NO₃)₂) freshly prepared using chilled DI water (150 cm³) was added. The mixture was blanketed with H₂ (101 kPa H₂, 50 cm³ min⁻¹; Airgas, UHP) and constantly stirred. After continuous stirring and exposure to the blanket of H₂ gas for 3 h, the supernatant was decanted. The solids were soaked in deionized water (30 cm³ g⁻¹) and decanted three times and then dried in stagnant air at 323 K for 12 h.

These specific conditions for electroless deposition were selected to maximize the fraction of Pd that deposits selectively onto supported Au nanoparticles and not elsewhere (e.g., the gas frit, or homogeneous precipitate). Note, we did not bubble H₂ into the suspension with a gas dispersion tube, because this procedure invariably deposited Pd onto the frit of the dispersion tube. In preliminary experiments, we observed that aqueous Pd(NO₃)₂ reduces readily in contact with H₂ to form monometallic Pd colloids in the absence of Au-SiO₂. Nucleation theory predicts this process depends superlinearly on the concentration of Pd-species,⁸⁵ while rates of electroless deposition are linear with precursor

Table 1. Mean Particle Sizes and Compositions of Pd and PdAu_x Catalysts

Catalyst	$\langle d \rangle_S$ (nm) ^a	$\langle d \rangle_N$ (nm) ^b	Standard Deviation (nm)	Au Con- tent (wt%) ^c	Pd Content (wt%) ^c	Atomic Ratio of Au to Pd ^c
Pd	3.9	3.3	1.0	-	0.052	0
Pd ₁ Au ₃	8.6	6.7	2.8	0.48	0.088	3
Pd ₁ Au ₁₈	9.5	7.3	2.8	2.0	0.059	18
Pd ₁ Au ₃₇	9.6	7.2	2.9	2.1	0.030	37
Pd ₁ Au ₅₀	9.4	7.5	2.7	2.1	0.022	50
Pd ₁ Au ₂₂₀	9.5	7.1	3.0	4.6	0.011	220

^a Determined by analysis of transmission electron microscopy images using Equation 1, ^b Simple average of particle sizes obtained by analysis of transmission electron microscopy images, ^c Determined by ICP-OES (Galbraith)

concentration and involve catalytic activation of H₂ on the pre-existing metal (i.e., Au) nanoparticles.⁸⁴ In addition, we anticipated that activation barriers to nucleate homogenous Pd particles would be greater than for Pd(NO₃)₂ reduction and deposition on Au surfaces. Consequently, we chose to minimize the temperature and lower Pd precursor concentration during the electroless deposition process to favor the deposition of Pd onto Au nanoparticles. As such, we used low Pd concentrations (≤ 0.2 mM Pd(NO₃)₂) and low temperatures (~ 273 K).

2.3. Synthesis of SiO₂ Supported Pd Nanoparticles

Monometallic Pd nanoparticles were formed on silica (0.05 % wt Pd-SiO₂) by a synthesis procedure that involves strong electrostatic adsorption.⁸⁶ An aqueous solution of Pd(NO₃)₂ was prepared with DI water (4.7 mM, 20 cm³). In a separate beaker, silica (20 g) was added to a mixture of DI water (350 cm³) and concentrated NH₄OH (50 cm³). The Pd(NO₃)₂ solution was added to the basic solution containing silica and stirred manually once every 30 min for 3 h. The solids were recovered, dried by vacuum filtration, and washed with DI water (500 cm³). Subsequently, the solids were loaded into a quartz boat and heated to 673 K at 3 K min⁻¹ in a flowing mixture of H₂ and He (20 kPa H₂, 81 kPa He, 100 cm³ min⁻¹) in a tube furnace and held at 673 K for 3 h.

Nanoparticles of Pd (e.g., 1-2 nm diameters) on silica agglomerate over the course of 8-10 hr during the direct synthesis reaction and form distributions of nanoparticles with larger mean diameters.⁷⁵ Therefore, we characterized monometallic Pd-SiO₂ by FTIR and TEM (*vide infra*) following steady state catalysis at relevant conditions (55 kPa H₂, 60 kPa O₂) for extended periods (> 12 h).

2.4. Analysis of Nanoparticle Sizes by Transmission Electron Microscopy and Volumetric CO Adsorption

The particle size distributions for each catalyst were evaluated by bright-field transmission electron microscopy using a JEOL 2010 LaB₆ operating at 200 kV. Samples were prepared by grinding the catalyst into a fine powder and dusting the powder onto copper-hole carbon TEM grids. Surface-averaged mean particle sizes were calculated using

$$\langle d \rangle_S = \frac{\sum_{i=1}^N d_i^3}{\sum_{i=1}^N d_i^2} \quad (1)$$

where d_i is the measured diameter of nanoparticle i and N is the total number of nanoparticles measured for any sample ($N > 300$). Conversely, number-averaged mean particle sizes, $\langle d \rangle_N$, are calculated as the simple average. Both values as well as the standard deviation for each catalyst are reported in Table 1. Surface-averaged calculations of mean particle size are more appropriate for catalysis applications because catalysis occurs at the nanoparticle surface. As such, surface-averaged diameters are used to estimate the numbers of surface atoms in each sample. Figure 1 presents a representative TEM image of the Pd₁Au₅₀ catalyst along with the particle size distribution for this material. The corresponding TEM images and particle size distributions for all other samples are presented in the Supporting Information (SI) (Section S3). Values of $\langle d \rangle_S$ for all PdAu_x catalysts are similar, which indicates that differences in catalytic properties cannot be explained by differences between the size of nanoparticles.

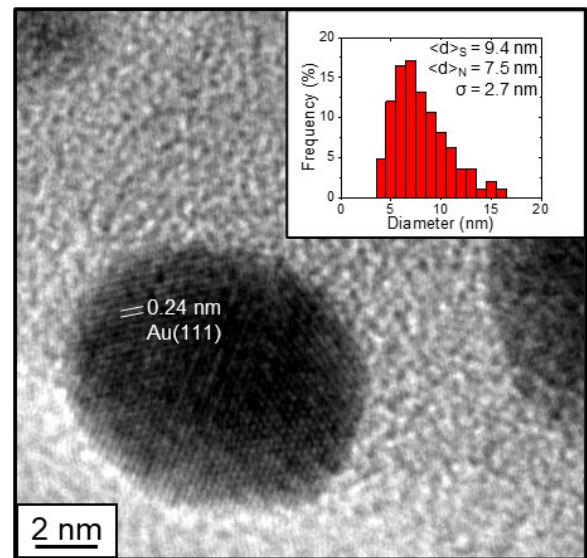


Figure 1. Representative TEM image of a Pd₁Au₅₀ nanoparticle showing lattice fringes consistent with Au(111). Inset shows particle size distribution for this catalyst.

2.5. Characterization of Catalysts by Fourier Transform Infrared Spectroscopy of Adsorbed CO

The relative numbers of Pd and Au atoms exposed on each nanoparticle, the type of atoms to which these were coordinated, and differences between the electronic states of surface Pd atoms were examined by comparisons of FTIR spectra of adsorbed ¹²CO and mixtures of adsorbed ¹²CO and ¹³CO. Samples were prepared by grinding catalysts (~60 mg) into a fine powder and pelletizing the powder into self-supporting ~20 mm diameter discs using a laboratory hydraulic press (Carver, Model C). These discs were set between two stainless steel retaining rings and loaded into a custom-built transmission IR cell with CaF₂ windows, described previously.^{41, 65, 87-89} The cell was sealed by compressing natural graphite ferrules (Chromalytic Technology Pty. Ltd.) with another stainless steel retaining ring on the cell exterior. Gaseous H₂, ¹²CO, He, and O₂ were introduced to the cell by digital mass flow controllers (Alicat, MC Series) mounted to a gas-handling manifold connected to the cell. In comparison, ¹³CO (Sigma-Aldrich, 99% ¹³C, <5% ¹⁸O) was introduced by pulses from a custom-mixed lecture bottle (10% ¹³CO in He). A short length of steel tubing was pressurized and each pulse of ¹³CO-He was released by briefly opening a ball valve.

Prior to adsorption of CO, all catalysts were pretreated in a combination of reductive and oxidative conditions to remove adventitious organic species and water. PdAu_x catalysts were pretreated by heating to 573 K at 10 K min⁻¹ in a flowing stream (30 cm³ min⁻¹) of O₂ (20 kPa) and He (81 kPa) and holding at 573 K for 1 h before cooling to 303 K in pure He. Samples were annealed in CO by heating to 383 K at 10 K min⁻¹ under flowing CO (1 kPa) and He (100 kPa), holding at 383 K for 1 h and cooling to 313 K still within 1 kPa CO. Monometallic Pd catalysts were pretreated by heating to 573 K at 10 K min⁻¹ in a flowing stream (30 cm³ min⁻¹) of H₂ (20 kPa) and He (81 kPa) and holding at 573 K for 1 h. The flow of H₂ was stopped and the sample was held under pure He flow (30 cm³ min⁻¹) for 30 min before cooling to 303 K under He.

Singleton frequencies ($\nu_0(^{13}\text{C}=\text{O})$) were measured by examining a series of infrared spectra of catalysts with surfaces saturated by mixed adlayers of ¹³CO-¹²CO with a wide range of ¹³CO to ¹²CO ratios at 303 K. This was achieved by first saturating the catalyst surface in ¹³CO and incrementally dosing small amounts of ¹²CO through short pulses with an MFC (0.01 cm³ min⁻¹). Surface coverages were estimated from peak intensities and peak centers were measured directly from the spectra. The metal loading and dispersion for 0.05 wt% Pd-SiO₂ material was too small for reliable singleton frequency measurement, so a 1.0 wt % Pd-SiO₂ material was synthesized by similar methods and sintered by calcination at 673 K for 4 h in air.⁸⁶ The 0.05 wt% and 1.0 wt% Pd-SiO₂ materials have similar surface-averaged mean diameters (~4 nm; Figure S3.1), though the 1.0 wt% catalyst does show a broader distribution. The two materials also show similar $\eta^1\text{-CO}^*\text{Pd}$ peak centers (Figure S6.3), which suggests that the singleton frequency measurement of the

1.0 wt% material is sufficiently representative of the 0.05 wt% material, especially when compared to PdAu_x.

2.6. Steady-State Formation Rate Measurements

Rates of H₂O₂ and H₂O formation were measured using a packed-bed reactor system that provides plug-flow hydrodynamics, as described elsewhere.^{41, 65, 66, 86} Catalyst (100-1000 mg) and SiO₂ (0-900 mg, for a total of 1000 mg catalyst and SiO₂) were loaded into a jacketed stainless steel reactor in between supporting glass wool and 4 mm diameter glass rods. Reactant gases (25% H₂ balance N₂ and 5% O₂ balance N₂ or 5% H₂ balance N₂ and UHP Air) were introduced to the system using digital mass flow controllers (Parker) and mixed with a stream of deionized and degassed H₂O (35 cm³ min⁻¹, >17.8 MΩ cm under Ar flow) fed in by an HPLC pump (SSI, M1-Class). Reaction temperatures were controlled using a refrigerated recirculating bath (Fisher Scientific, Isotemp) to flow a 50% v/v aqueous ethylene glycol solution through the reactor cooling jacket and monitored by a k-type thermocouple embedded in the reactor jacket. The reactor pressure was set by a back-pressure regulator (BPR, Equilibar, EB1LF1-SS316) controlled by an electronic pressure reducer (EPR; Proportion Air, QB1S). The reactor effluent was split into a gas and a liquid stream using a polyvinyl chloride gas-liquid separator. The H₂ conversion was measured by analysis of the gas stream by gas chromatography (Agilent, 7890, TCD, Ar carrier and reference gas) with a packed column (Sigma-Aldrich, 3 m x 2.1 mm, molecular sieve 5A) and using N₂ as an internal standard. Samples were taken every 10 min from the liquid stream using an electronically actuated valve (Banjo Corp., LEV025PL) to deliver liquid to an electronic 10-port valve (Vici) which injected 1.0 cm³ of sample along with 1.0 cm³ of a colorimetric indicator (6 mM neocuproine, SageChem, ≥98%; 4.1 mM CuSO₄, VWR, ≥98%; 25% v/v ethanol, Decon Laboratories Inc., 100%) into test tubes held in an automated fraction collector (Biorad, 2110). The samples were then analyzed by a visible light spectrometer (Spectronic, Genesys 20, 454 nm) to determine H₂O₂ concentrations by comparison with calibration curves obtained using samples of known H₂O₂ concentration.

The effects of H₂ and O₂ pressure or temperature on product formation rates were only examined after achieving steady-state conversion for each sample, which was defined as when selectivity became invariant with time on stream (typically > 3 h). In this study, selectivity is defined as the measured rate of H₂O₂ production divided by the rate of H₂ consumption.

Catalyst deactivation was corrected for by linear interpolation of time-on-stream data. Deactivation was typically small (~1% hr⁻¹). Analysis of spent PdAu catalysts provide no evidence of leaching or sintering with time-on-stream. Further, *in situ* XAS indicates that the catalysts restructure on a short (< 1 h) timescale, therefore, catalyst deactivation cannot be caused by replacement of surface Pd with Au. Trace organic contaminants (~1 nM) present in the solvent may be responsible for the loss of rates. Turnover rates for H₂O₂ and H₂O formation were obtained by normalizing measured product formation rates by the number of Pd atoms exposed at the surface of nanoparticles (Pd_s). Monometallic Au nanoparticles form negligible quantities of H₂O₂

under these conditions (Figure S4.1), likely because Au does not activate H₂ readily at these conditions.⁹⁰ Consequently, we conclude that exposed Pd atoms participate in the kinetically relevant steps for both H₂O₂ and H₂O formation. To estimate the value of Pd_s for each catalyst, we used dispersion values calculated from TEM-derived mean cluster diameters and assumed that Pd completely segregates to the surface of the nanoparticles during catalysis.

2.7. X-ray Absorption Spectroscopy Analysis of Pd Coordination

The electronic properties and local structure of Pd and PdAu catalysts were evaluated by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements at the Pd K-edge (24350 eV) obtained using a 100-element Ge monolith fluorescence detector (Canberra) at Beamline 9-3 of the Stanford Synchrotron Radiation Light Source (SSRL). This beamline is a 16-pole, 2-Tesla wiggler side station with vertically collimating mirror for harmonic rejection and a cylindrically bent mirror for focusing. The photon energy was selected using a liquid-nitrogen-cooled, double-crystal Si (220) $f = 90^\circ$ monochromator to scan between 24,100-25,100 eV. The catalyst (100 mg) was crushed to 80-120 mesh and loaded into a glassy carbon reactor (4.1 mm inner diameter, HTW Hochtemperatur-Werkstoffe GmbH) using glass wool as a mechanical support. The glassy carbon reactor was inserted into an *in situ* XAS cell⁹¹ affixed to a manifold used to deliver either gas (H₂, O₂) or H₂O (10 cm³ min⁻¹) saturated with gas (H₂, O₂).⁷⁵ The gas composition was controlled by mass flow controllers (Parker Porter, 601), which allowed gas to flow through gas dispersion frits (40-60 μ m) into two pressurized saturation units (Swagelok, 304L-HDF8-2250) filled with deionized H₂O that could be operated at pressures above 6 MPa. Two HPLC pumps (SSI, M1 Class) were used to mix streams of saturated H₂O from each reservoir and deliver the mixed stream containing the desired concentrations of H₂ and O₂ to the cell. The pressures of each saturator and the *in situ* cell were controlled independently by dedicated back-pressure regulators (Andon Specialties, BP3-1A11QCK11L). The XAS data for the monometallic Pd catalyst are adapted from prior work,⁷⁵ which used a Pd-SiO₂ catalyst synthesized in a similar manner and with comparable metal loadings.

All XAS measurements were made at room temperature. Prior to XAS measurements under H₂O₂ synthesis conditions, catalysts were scanned in ambient air. Each *in situ* measurement was initiated by subsequently introducing H₂- and O₂-saturated water to the reactor *via* the HPLC pumps. A minimum of three spectra were collected at each set of conditions, and the spectra found to be at steady-state were merged and aligned using Pd foil reference spectra collected simultaneously. Values of $\chi(k)$ were obtained by subtracting smooth atomic background from the normalized absorption coefficient using the AUTOBK code (where k is the photoelectron wave number). The theoretical EXAFS signal for Pd-O, Pd-Pd, Pd-Au scattering paths were constructed using the FEFF6 code.⁹² A fcc crystal structure with

a lattice constant of 3.89 Å was used to model Pd. The Pd-Au structure was constructed by replacing all the Pd atoms in the first shell of the Pd fcc structure by Au atoms. A Pd acetate trimer structure was used for Pd-O.⁹³ The theoretical EXAFS signals were fitted to the data in R -space using the Artemis program of the Demeter package using simultaneous k -weights of 1, 2, and 3. The spectra were fitted by varying the coordination number of the single scattering Pd-O and Pd-M paths (where M = Pd, or Au), the bond length disorder, the effective Pd-O/M scattering lengths and the correction to the threshold energy, ΔE_0 . The value for the passive electron reduction factor (S_0^2) was obtained by first analyzing the spectrum for a Pd foil, and the best fit value (0.76) was fixed during the fitting. The k -range used for fourier transform of the $\chi(k)$ was 2.6-13 Å⁻¹ and the R -range for fitting was 1.2-3.1 Å. The best parameters fit using k -weights of 1, 2, 3 (simultaneously) in Artemis are reported, however, the results were similar to those using only a k -weight of 2. Additionally, the k -range did not have a significant effect on the best fit values of the model fit but did affect their uncertainties.

2.8. Computational Methods

First-principle density functional theory calculations were carried out to determine the energetics for the elementary adsorption, desorption and surface reaction paths for H₂O₂ and H₂O formation over PdAu alloy surfaces within aqueous media. The calculations in the condensed phase were carried out using a density of ~ 1 g cm⁻³ for water in the unit cell. *Ab initio* molecular dynamics simulations were carried out for greater than 5 ps to allow the explicit water molecules to relax around the reacting molecules and generate stable reactant structures. These low energy structures along the molecular dynamics' trajectory were used to establish representative model structures to conduct subsequent static density functional theory (DFT) calculations to determine the reaction energies and activation barriers.

All of the simulations were carried out using plane wave DFT as implemented in the Vienna ab-initio simulation program (VASP).⁹⁴⁻⁹⁶ Plane waves were constructed with an energy cutoff of 396 eV along with projector augmented wave potentials (PAW) to model interactions between core and valence electrons.^{97, 98} The generalized gradient approximation (GGA) along with the Perdew-Burke-Ernzerhof (PBE) functional were used to determine the exchange and correlation gradient corrections and D3 method of Grimme was used to characterize van der Waals interactions and capture the dispersive interactions in the local environment.⁹⁹⁻¹⁰¹

Wavefunctions were optimized in a self-consistent manner and converged to within 10⁻⁶ eV using a Gamma centered 3 x 3 x 1 k-point mesh grid. The atomic positions were optimized and converged to a point where the maximum force on each atom was less than 0.1 eV Å⁻¹. A two-step approach was used to isolate the transition states and calculate the activation barriers.

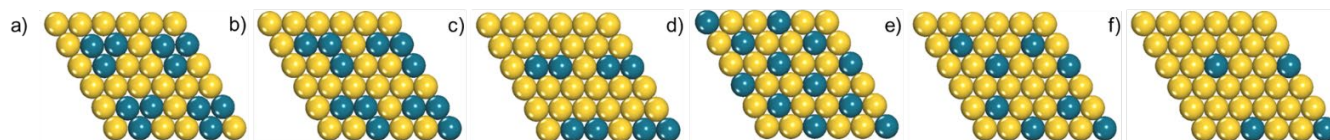


Figure 2. Pd atom distributions on Au (111) slabs that include (a) equilateral closed-packed Pd trimers, (b) open Pd trimers, (c) Pd dimers, (d) paired Pd monomers with six Pd next-nearest neighbors (NNN=6), (e) paired Pd monomers with three Pd next-nearest neighbors (NNN=3), and (f) isolated Pd monomers with exclusively Au atoms at nearest and next-nearest neighbor positions (NNN = 0).

The first step used the climbing nudged elastic band (NEB) method to optimize the energies for a series of structures along the reaction path using a force tolerance of $0.1 \text{ eV } \text{\AA}^{-1}$. The highest energy structures were subsequently used as input to dimer method to isolate the transition state structures and were converged until the forces dropped below $0.08 \text{ eV } \text{\AA}^{-1}$.¹⁰²⁻¹⁰⁴

2.9. Creation of Model Surfaces

To discern the catalytic consequences of isolating Pd atoms in Au, reaction energies and activation barriers for the formation of H_2O_2 and H_2O (by decomposition of OOH^*) from H_2 and O_2 on six different surfaces comprised of Au and Pd atoms were calculated. Figure 2 shows the model surfaces examined, which include predominantly Au slabs that contains Pd trimers (Figures 2a-2b) or dimers (Figure 2c) and three different forms of Pd monomers (Figures 2d-2f). Comparisons between reaction energies and barriers calculated on these surfaces reflect the effects of differences in the nearest-neighbor Pd-Pd coordination number (NN, $1 \leq \text{NN} < 2$) and in the next nearest-neighbor Pd-Pd coordination number (NNN, $0 \leq \text{NNN} \leq 6$) on O_2 reduction. Among these models, a single Pd atom with NN and NNN values equal to zero (Figure 2e) was selected to represent the behavior of the most dilute PdAu_x surfaces.

While previous studies suggest that high coverages of oxygen on Pd surfaces significantly modify energy barriers to promote H_2O_2 formation,^{75, 105, 106} *in situ* characterization of PdAu surfaces (Section 3.2) suggests that such high coverages do not form under the studied conditions. Additionally, the differing numbers of Pd atoms in the model slabs (Figure 2) complicate consistent interpretation of coverage effects for all coverages other than zero; as such reaction barriers and energetics are calculated considering an otherwise empty surface.

All calculations were carried out using periodic slabs consisting of a 3×3 unit cell with four layers of the Au(111) surface by replacing surface Au atoms with Pd atoms according to the above description and optimizing the metal slab before adding the solvent layers. The bottom two layers of the slab were held fixed at bulk positions of the Au lattice, while the top two layers were allowed to relax fully. A vacuum region of $\sim 15 \text{ \AA}$ between the topmost and bottom metal layers was used in all the condensed phase calculations to allow the solvent molecules to relax.

The densities of states (DOS) for the different surfaces examined herein were calculated in two steps. In the first step, structural optimizations and single point energy calculations for the slab were carried out using a k-point grid of $6 \times 6 \times 1$ with an energy convergence of 10^{-6} eV and until the

force on each atom was below 0.05 eV . In the second step, the DOS was calculated using a higher k-point grid of $12 \times 12 \times 1$. The *d*-band center reported was calculated as the first moment of the *d*-band. The data for a Pd(111) surface are adapted from reference 75, which employed identical methods to calculate DOS.

3. Results and Discussion

3.1. Effect of Au to Pd Ratio within Nanoparticles on Rates and Selectivities for H_2O_2 Formation

To understand the effects of dispersing Pd atoms on Au nanoparticles, we measured primary H_2O_2 formation rates and selectivities across the series of uniform Pd and Pd_1Au_x nanoparticle catalysts ($0 \leq x \leq 220$) supported on silica. Figure 3 shows that both turnover rates for H_2O_2 formation and the H_2O_2 selectivities depend on the atomic ratio of Au to Pd across this series of catalysts (55 kPa H_2 , 60 kPa O_2 , 286 K). H_2O_2 turnover rates decrease by three-fold (0.37 to $0.12 \text{ mol H}_2\text{O}_2 \text{ mol Pd}^{-1} \text{ s}^{-1}$) across this range of materials as the ratios of Au to Pd increase. Measured turnover rates generally decrease but possess noticeable scatter with the addition of Au, which arises from significant uncertainty in estimates for the number of active sites on these materials (Supporting information section S5). To circumvent this complication, we focus primarily on kinetic parameters that do not depend upon estimates for the number of sites including H_2O_2 selectivities, apparent activation enthalpies, and changes in rates as functions of reactant concentrations. These decreases in H_2O_2 turnover rates coincide with a nearly monotonic increase in H_2O_2 selectivities ranging from $19 \pm 1\%$ for Pd to $95 \pm 3\%$ for $\text{Pd}_1\text{Au}_{220}$. Nanoparticles of Pd_1Au_3 deviate from this trend and provide H_2O_2 selectivities ($15 \pm 1\%$) slightly lower than monometallic Pd ($19 \pm 1\%$); these Pd_1Au_3 nanoparticles predominantly expose Pd atoms at their surfaces with Au-rich subsurfaces, and therefore, possess significant surface Pd-Pd coordination (*vide infra*) with electronic modifications caused by the Au subsurface. Larger atomic ratios of Au to Pd ($x > 18$) provide significant increases in H_2O_2 selectivities, and this nonmonotonic trend suggests that Au influences the reactivity of Pd in multiple ways. These H_2O_2 selectivities are lower than previous reports of catalysts with similar elemental compositions,^{39, 41, 45, 56, 57, 107} which likely originates from differences in the experimental conditions (i.e., temperature, solvent composition, promoters, reactor type). For example, many studies implement alcohol solvents and one or more forms of promoters (e.g., mineral acids^{59, 60} and halides^{59, 61, 62}) that frequently increase H_2O_2 selectivities but complicate fundamental investigations. The results in Figure 3 suggest that the increases in primary H_2O_2 selectivities and decreases in turnover rates may reflect differences in the

structural motifs of Pd active sites, the electronic characteristics of these active sites, or the mechanism of the reactions that produce H_2O_2 and H_2O among these six catalysts as a result of changes in the Au to Pd atomic ratio. We examine these possibilities using X-ray absorption spectroscopy, detailed measurements of catalytic rate as functions of reactant concentrations and temperature, and *ab initio* quantum calculations on representative model surfaces in the presence of the solvent.

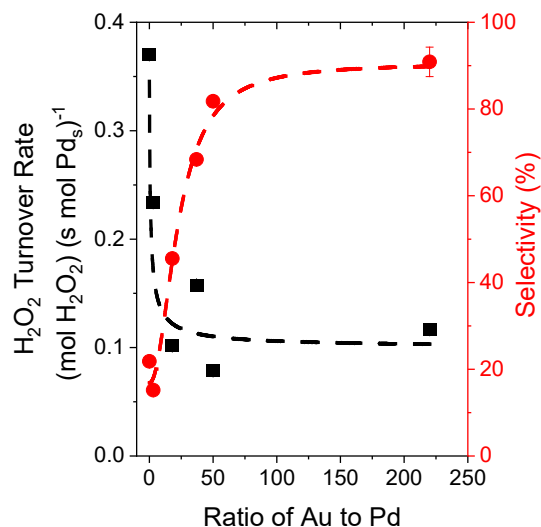


Figure 3. Steady-state H_2O_2 turnover rates (■) and primary H_2O_2 selectivities (●) for PdAu_x catalysts with a range of Au

to Pd atomic ratios ($0 \leq x \leq 220$) at standard conditions (55 kPa H_2 , 60 kPa O_2 , 286 K).

3.2. Characterization of Pd Coordination by X-Ray Absorption Spectroscopy

Figure 4 shows the *ex situ* Pd K-edge XANES spectra, FT-EXAFS in *R*-space, and EXAFS best-fit coordination numbers for each catalyst obtained from catalysts previously subjected to oxidative thermal treatments (1 h, 5 K min^{-1} , 573 K, 100 $\text{cm}^3 \text{min}^{-1}$ air) and held within ambient conditions (air, ~ 295 K). The normalized XANES spectra (Figure 4a) show a slightly lower whiteline intensity for materials with high Au to Pd (0.98 for $\text{Pd}_1\text{Au}_{220}$) ratios in comparison to Pd (1.07) and Pd_1Au_3 (1.03). In addition, the amplitude of the oscillations above the K-edge indicates that Pd atoms in the PdAu_x materials possess lower total coordination numbers than in monometallic Pd nanoparticles or Pd foil, which implies that Pd exists predominantly at the surfaces of the nanoparticles. Analysis of all *ex situ* spectra show a large amount of Pd-O coordination that results from the oxidative pretreatment and exposure to air while collecting spectra. The average Pd-O coordination number decreases as the Au to Pd ratio increases (e.g., $N_{\text{Pd-O}} = 3$ on Pd_1Au_3 and $N_{\text{Pd-O}} = 0.5$ on $\text{Pd}_1\text{Au}_{220}$), and intensities of XANES white lines decrease simultaneously (Figure 4a). These changes suggest that coordination of Pd to Au reduces the propensity of Pd to oxidize. Taken together, the low Pd-Pd and Pd-Au coordination numbers and significant Pd-O coordination indicate that the Pd_1Au_3 and $\text{Pd}_1\text{Au}_{18}$ catalysts contain segregated domains of oxidized Pd on the exterior of Au nanoparticles.

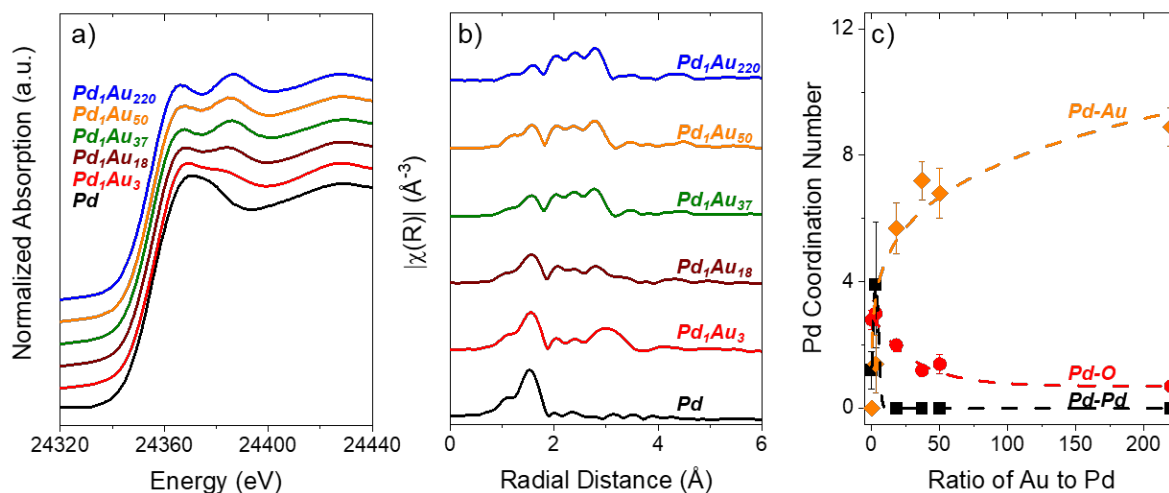


Figure 4. (a) XANES spectra and (b) EXAFS magnitude of the Fourier transformed k^2 -weighted $\chi(k)$ data ($k = 2.7\text{--}13 \text{ \AA}^{-1}$) for Pd (—), Pd_1Au_3 (—), $\text{Pd}_1\text{Au}_{18}$ (—), $\text{Pd}_1\text{Au}_{37}$ (—), $\text{Pd}_1\text{Au}_{50}$ (—) and $\text{Pd}_1\text{Au}_{220}$ (—) and (c) EXAFS best fit Pd-Pd (■), Pd-Au (◆) and Pd-O (●) coordination as a function of the atomic ratio of Au to Pd measured *ex situ* (ambient air, 298 K).

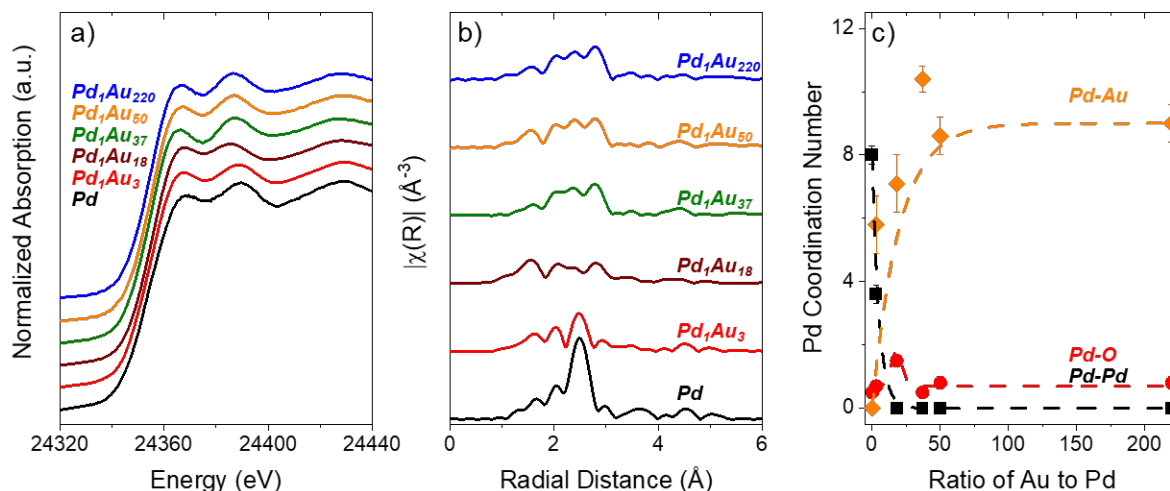


Figure 5. (a) XANES spectra and (b) EXAFS magnitude of the Fourier transformed k^2 -weighted $\chi(k)$ data ($k = 2.7$ - 13 \AA^{-1}) for Pd (—), Pd₁Au₃ (—), Pd₁Au₁₈ (—), Pd₁Au₃₇ (—), Pd₁Au₅₀ (—) and Pd₁Au₂₂₀ (—) and (c) EXAFS best fit Pd-Pd (■), Pd-Au (◆) and Pd-O (●) coordination numbers as a function of the atomic ratio of Au to Pd measured *in situ* (55 kPa H₂, 60 kPa O₂, 298 K).

These results demonstrate that the extent of alloying depends strongly on composition under oxidizing conditions. The direct synthesis of H₂O₂ requires a combination of H₂ and O₂ co-reactants, and consequently, the structure and chemical states of Pd and PdAu_x nanoparticles may change in response. Figure 5 shows results from *in situ* XANES and EXAFS that reveal that the structure of these Pd and PdAu_x catalysts at relevant conditions (55 kPa H₂, 60 kPa O₂, 298 K) differs significantly from those observed *ex situ*. The *in situ* XANES results (Figure 5a) show a decrease in the white-line intensity of the monometallic Pd and Pd₁Au₃ catalysts only and all have similar white line intensity. Additionally, the magnitude of the EXAFS spectra (Figure 5b) and the Pd coordination numbers (Figure 5c) differ considerably from observations made *ex situ*. Differences between *ex situ* and *in situ* XAS of the Pd and Pd₁Au_x nanoparticles demonstrate that the reaction conditions decrease values of $N_{\text{Pd-O}}$ and reduce Pd to a predominately metallic state, which agrees with prior *in situ* XAS performed on Pd and PdAu nanoparticles during direct synthesis.^{74,75} Values of $N_{\text{Pd-Au}}$ measured *in situ* exceed those obtained *ex situ* for each Pd₁Au_x material, which demonstrates that these reaction conditions cause Pd to alloy with Au once Pd reduces suggesting that Pd could be segregated on the surface of Au as PdO_x domains. Across the series of Pd₁Au_x materials, $N_{\text{Pd-Au}}$ initially increases with the atomic ratio of Au to Pd from a value of 6 for Pd₁Au₃ to values near 9 for Pd₁Au₃₇ and above. Coordination between Pd atoms cannot be detected (i.e., $N_{\text{Pd-Pd}} \sim 0$) for any bimetallic material aside from Pd₁Au₃. Consequently, the total coordination number for Pd falls between 7 – 10 for all Pd₁Au_x materials, which is significantly lower than the coordination number of Pd in the bulk of a face centered cubic structure ($N_{\text{Pd-Pd}} = 12$). These results indicate that the majority of Pd atoms reside at the surfaces of Pd₁Au_x nanoparticles, which agrees with prior experimental and theoretical studies that examined the structure of PdAu alloys in the presence of O₂.¹⁵⁻¹⁷ Figure 5c shows that most PdAu catalysts possess $N_{\text{Pd-O}}$ values near or slightly less than

one, which suggests that oxygen-derived intermediates may saturate these Pd sites during catalysis (*vide infra*). The data for Pd₁Au₁₈ deviate slightly from the trends observed in the other Pd₁Au_x catalysts, which suggests differences in structure between this material and the other Pd₁Au_x materials. The Pd₁Au₁₈ catalyst shows no measurable Pd-Pd coordination and greater $N_{\text{Pd-O}}$ than the other Pd₁Au_x catalysts *in situ*; however, $N_{\text{Pd-Pd}}$ becomes 0.7 after reductive treatments (Table S7.3). This comparison suggests that the segregated domains of oxidized Pd on Au persist in this catalyst under reaction conditions.

Taken together, the Pd coordination numbers obtained *in situ* (Figure 5c) strongly suggest that surfaces of Pd₁Au₃₇, Pd₁Au₅₀, and Pd₁Au₂₂₀ catalysts primarily consist of Au with very low mole fractions of Pd. Within these surfaces, Pd primarily exists as monomers and possibly a few Pd nearest neighbors that could not be detected by EXAFS due to their low concentration compared with Pd-Au. As such, these nanoparticles form single atom alloys during catalysis. The differences in turnover rates for the formation of H₂O₂ and H₂O and the selectivities towards H₂O₂ for this series of Pd and Pd₁Au_x catalysts (Figure 3) likely reflect the changes in coordination number for Pd observed *in situ* (Figure 5). However, rates and selectivities differ between Pd₁Au₃₇, Pd₁Au₅₀, and Pd₁Au₂₂₀ despite the strong similarities in the structure of these materials determined by EXAFS. However, a comparison of the XANES spectra in Figure S7.2 show measurable differences at 24375 eV suggesting that the Pd environment is slightly modified as the Au to Pd ratio increases. EXAFS analysis of the next nearest neighbors was dominated by Pd-Au scattering and resulted in large uncertainties for the number of Pd atoms in the second coordination shell. Consequently, we hypothesize that next nearest neighbor interactions (i.e., the second coordination shell of Pd atoms in Au), which challenges EXAFS analysis, appear to impact catalysis. To test this hypothesis, we developed an experimental approach to examine structure and proximity of exposed Pd atoms beyond the first coordination shell.

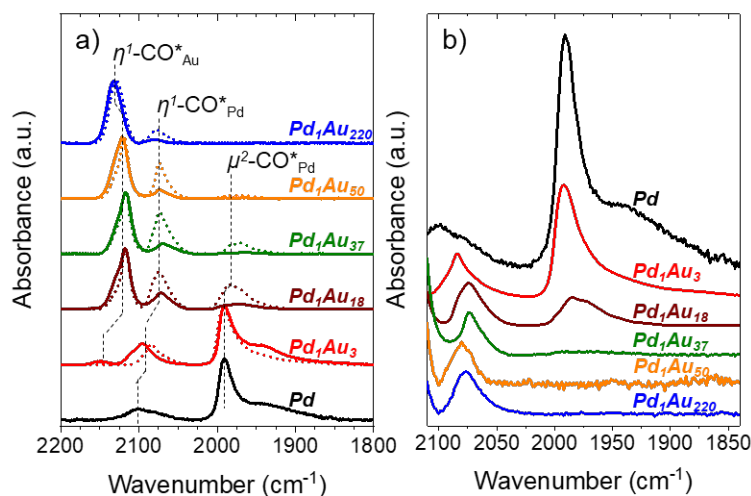


Figure 6. Infrared spectra of CO*-saturated surfaces of Pd (—), Pd₁Au₃ (—), Pd₁Au₁₈ (—), Pd₁Au₃₇ (—), Pd₁Au₅₀ (—) and Pd₁Au₂₂₀ (—) catalysts (0.02 kPa CO, 303 K). (a) Spectra following initial CO exposure (solid lines) and after annealing in CO (dashed lines; 1 h, 1 kPa CO, 373 K). All spectra normalized by the maximum intensity. (b) Infrared spectra after annealing in CO (1 kPa CO, 373 K, 1 h) normalized by the intensity of the η^1 -CO*_{Pd} feature.

3.3. Analysis of Pd and PdAu_x Nanoparticle Structure by Infrared Spectra of Adsorbed CO

Figure 6 shows steady-state infrared spectra of CO adsorbed to the surfaces of Pd and Pd₁Au_x catalysts (0.02 kPa CO, 303 K) following *in situ* oxidative (20 kPa O₂, 573 K, 1 h) or reductive (1 kPa CO, 373 K, 1 h for PdAu_x, and 20 kPa H₂, 673 K, 1 h for Pd) treatments designed to change the segregation and dispersion of Pd atoms at the surface. These treatments consistently yield infrared spectra that show three distinct binding configurations for CO*. Absorption features between 2130 - 2110 cm⁻¹ correspond to CO linearly bound to Au atoms (η^1 -CO*_{Au}), peaks between 2100 and 2070 cm⁻¹ arise from CO linearly bound atop Pd atoms (η^1 -CO*_{Pd}), and peaks below 2000 cm⁻¹ reflect CO adsorbed at bridge (μ^2 -CO*_{Pd}) and three-fold hollow (μ^3 -CO*_{Pd}) sites formed by ensembles of Pd atoms.^{19, 33, 40, 42, 43, 45, 108}

After oxidative treatments, the FTIR spectra of adsorbed CO show clear differences between the catalysts. Across the series of materials, the peak areas of η^1 -CO*_{Au} relative to η^1 -CO*_{Pd} and μ^2 -CO*_{Pd} increase with the Au to Pd ratio, reflecting increasing enrichment of surfaces with Au. The η^1 -CO*_{Pd} peak redshifts by ~27 cm⁻¹ between Pd to Pd₁Au₃₇, which agrees with redshifts attributed to a mixture of ligand and ensemble effects in prior studies.^{42, 43, 109} We analyze differences in η^1 -CO*_{Pd} features in greater detail later (Section 3.4). The Pd₁Au₃₇, Pd₁Au₅₀ and Pd₁Au₂₂₀ catalysts show little or no μ^2 -CO*_{Pd}, which suggests that these materials predominantly expose atomically disperse Pd after oxidative treatments, which agrees with the interpretation of Pd coordination numbers derived from EXAFS (Section 3.2). In contrast, the spectrum for Pd₁Au₃ shows a combination of a μ^2 -CO*_{Pd} and a η^1 -CO*_{Pd} feature, the combined area of which exceeds that for η^1 -CO*_{Au} by a factor of 45, which indicates that Pd₁Au₃ nanoparticles predominantly expose Pd and few Au atoms and may resemble core-shell structures.

Reductive treatments in CO (1 kPa CO, 373 K, 1 h) induce significant structural changes that appear in the vibrational features of CO* subsequently adsorbed (Figure 5; 0.02 kPa,

303 K). The reductive treatment increase the peak area of η^1 -CO*_{Pd} and μ^2 -CO*_{Pd} and decreases the intensity of η^1 -CO*_{Au} for all PdAu_x nanoparticles relative to spectra obtained after oxidative treatments. These changes demonstrate that CO exposure at moderate temperature enriches PdAu_x nanoparticle surfaces in Pd. On Pd₁Au₃, the η^1 -CO*_{Pd} feature redshifts by 12 cm⁻¹ and peaks for η^1 -CO*_{Au} and μ^3 -CO*_{Pd} (shoulder at 1940 cm⁻¹) disappear as a consequence of restructuring. This redshift in η^1 -CO*_{Pd} exceeds the shift caused by dipole coupling alone (*vide infra*, Figure 7), which signifies a change in the electronic structure of the exposed Pd atoms in this catalyst. The other PdAu_x catalysts present shifts in the η^1 -CO*_{Pd} feature of 2 cm⁻¹ or less, representing small differences in dipole-dipole coupling or electronic structure of Pd. The thermal treatment also causes the Pd₁Au₃₇ and Pd₁Au₅₀ catalysts to show detectable amounts of μ^2 -CO*_{Pd}, which is consistent with the change in EXAFS for Pd₁Au₁₈ under a CO atmosphere (Table S7.3) and demonstrates that Pd oligomers form at the surfaces of these materials. This results from the increased coverage of Pd atoms and the greater stability of μ^2 -CO*_{Pd} and μ^3 -CO*_{Pd} configurations that involve Pd dimers and oligomers in comparison to η^1 -CO*_{Pd} on bimetallic PdAu_x surfaces.¹¹⁰⁻¹¹²

The relative populations of monomeric and oligomeric Pd atoms on surfaces of Pd₁Au_x nanoparticles and their sensitivity to the chemical environment can be examined by quantifying the ratio (ρ) of areas for features corresponding to η^1 -CO*_{Pd} and μ^2 -CO*_{Pd} prior to annealing in CO (after only oxidative or reductive treatments, Section 2.5) and following treatments in CO (1 kPa CO, 373 K, 1 h). Table 2 shows that values of ρ for Pd and Pd₁Au_x materials increase monotonically with the Au to Pd ratio regardless of the pretreatment conditions.

Table 2. Ratio (ρ) of η^1 -CO*_{Pd} to μ^2 -CO*_{Pd} peak area for Pd and PdAu_x catalysts before and after annealing in CO.

Catalyst	ρ
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	Before annealing in CO ^{a,b}	After annealing in CO ^{a,c}
Pd	0.1	n. a.
Pd ₁ Au ₃	0.3	0.3
Pd ₁ Au ₁₈	1.8	1.0
Pd ₁ Au ₃₇	7.9	5.7
Pd ₁ Au ₅₀	>50 ^d	14
Pd ₁ Au ₂₂₀	>50 ^d	>50 ^d

^aMeasured in 0.02 kPa CO at 303 K ^bPretreated in 20 kPa O₂, 573 K, 1 h for PdAu_x or in 20 kPa H₂, 573 K, 1 h for Pd ^cPretreated in 1 kPa CO, 373 K, 1 h ^dThese spectra show no detectable μ^2 -CO*_{Pd}; reported values are instead lower bounds estimated from the signal-to-noise ratios of each spectra.

Values of ρ decrease following treatment in CO for PdAu_x materials with Au to Pd ratios of 18 and greater, because CO* stabilizes greater fractions of Pd at the surfaces of these nanoparticles. Among these CO treated nanoparticles, ρ consistently increases with the Au to Pd ratio and becomes greater than 50 for Pd₁Au₂₂₀, which suggests that Pd exists predominantly as monomers after reduction in CO for this material only. These trends agree with expectations from Monte Carlo simulations that account for differences in the stability of Pd-Pd and Pd-Au bond strengths in predictions for the distribution of Pd atoms among monomeric and oligomeric surface species as functions of the fractional coverage of Pd in equilibrated PdAu(111) surfaces.^{50,51} Hence the decrease in ρ and increase in η^1 -CO*_{Au} area, relative to both η^1 -CO*_{Pd} and μ^2 -CO*_{Pd}, shows that the Pd surface coverage decreases systematically with increases in the Au to Pd ratio. *In situ* XAS, however, indicates that nearly all Pd atoms within the Pd₁Au₃₇, Pd₁Au₅₀ and Pd₁Au₂₂₀ catalysts reside on the nanoparticle surface as monomers (i.e., $N_{\text{Pd-Pd}} \sim 0$) (Figure 5). Consequently, these comparisons between XAS and FTIR of CO* species suggest that the separation between Pd monomers increases with the Au to Pd ratio.

3.4. Probing Changes in Geometric and Electronic Structure of Exposed Pd Atoms *via* Infrared Spectra of Mixed ¹²CO and ¹³CO Adlayers

Values of the vibrational frequencies measured for the $\nu(\text{C=O})$ mode of CO*-species on transition metal surfaces depend upon the extent of electron donation and back-donation between CO and the metal surface but also dipole-dipole coupling between adsorbed CO molecules (i.e., the vibrational Stark effect).^{12, 113} These effects can be deconvoluted by independently changing the significance of dipole-dipole coupling between CO*-species by the adsorption of mixtures of ¹³CO and ¹²CO.^{11, 12} As one example, the individual contributions of electron exchange with the surface and the magnitude of dipole-dipole coupling can be assessed by measuring changes in the frequency of $\nu(^{13}\text{C}=\text{O})$ for η^1 -CO*_{Pd} as a function of fractional coverage of ¹³CO ($\theta_{^{13}\text{CO}}$) in a saturated monolayer of ¹²CO and ¹³CO (i.e., $\theta_{^{12}\text{CO}} + \theta_{^{13}\text{CO}} = 1$).^{12, 114} This analysis uses the relationship:

$$\nu(^{13}\text{C}=\text{O}) = \nu_0 + \theta_{^{13}\text{CO}}\Delta\nu \quad (2)$$

where the intercept ν_0 represents the singleton frequency (i.e., $\nu(^{13}\text{C}=\text{O})$ in the absence of dipole-dipole coupling) and reports on the electronic structure of the binding site, and $\Delta\nu$ quantifies the shift caused by dipole-dipole coupling, which depends on the inverse-cube of distance between comparable CO*-species.^{113, 114}

Figure 7 shows that values of $\nu(^{13}\text{C}=\text{O})$ depend linearly upon $\theta_{^{13}\text{CO}}$ for the Pd and Pd₁Au_x catalysts after oxidative treatments (20 kPa O₂, 573 K, 1 h), which agrees with the form of equation 2. In each experiment, the nanoparticle surfaces were initially saturated with ¹³CO*, which was subsequently displaced using small pulses of ¹²CO (Section 2.5.). Our analysis considers η^1 -CO* on Pd, because this feature appears on all catalysts and can be readily deconvoluted from the other peaks present. The values of ν_0 do not depend monotonically on the ratio of Au to Pd (Table 3) however, nanoparticles with Au to Pd ratios of 18 and greater exhibit lower values than pure Pd.

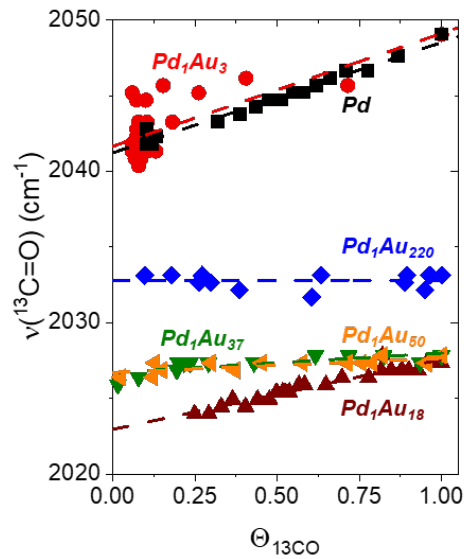


Figure 7. The vibrational frequency for the $\nu(\text{C=O})$ mode of η^1 -¹³CO*_{Pd} as a function of the fractional coverage of ¹³CO* on monometallic Pd (■), Pd₁Au₃ (●), Pd₁Au₁₈ (▲), Pd₁Au₃₇ (▼), Pd₁Au₅₀ (◀) and Pd₁Au₂₂₀ (◆) at 303 K. Dashed lines indicate linear fits to data.

These comparisons show that the interactions between Pd and Au clearly induce an electronic modification to the Pd present at the surface and resemble findings from similar measurements made on PdAu/Pd(111) single crystal surface alloys at 290 K.¹¹⁵ Singleton frequency shifts from 2041 cm⁻¹ for monometallic Pd to 2023 cm⁻¹ for Pd₁Au₁₈, but further increases of the catalyst Au content cause an increase of the singleton frequency to 2033 cm⁻¹ for Pd₁Au₂₂₀. These observations seem consistent with non-monotonic changes in the Pd *d*-band structure with surface Au content observed by core-level XPS of PdAu films annealed at various temperatures²¹ and Pd K-edge whiteness intensities of carbon-supported PdAu nanoparticles with Au to Pd ratios between zero and five.¹¹⁶ Comparing the PdAu_x catalysts with Au to

Pd ratios of 18 to 50, the values of ν_0 are too similar to adequately differentiate the catalysts. The Pd₁Au₂₂₀ catalyst shows a slightly higher ν_0 (2033 cm⁻¹), which may imply a slightly different electronic structure of the Pd atoms in this sample, though the direct effect of this difference on catalysis cannot be ascertained from this measurement alone.

Table 3. Dipole coupling shifts ($\Delta\nu$) and singleton frequencies (ν_0) of η^1 -¹³CO*_{Pd} for Pd and PdAu_x catalysts

Catalyst	$\Delta\nu$ (cm ⁻¹)	ν_0 (cm ⁻¹)
Pd	7.3 ± 0.2	2041 ± 1
Pd ₁ Au ₃	7.5 ± 1.3	2042 ± 1
Pd ₁ Au ₁₈	4.6 ± 0.3	2023 ± 1
Pd ₁ Au ₃₇	1.3 ± 0.4	2027 ± 1
Pd ₁ Au ₅₀	0.9 ± 0.2	2027 ± 1
Pd ₁ Au ₂₂₀	0.0 ± 0.4	2033 ± 1

The values of $\Delta\nu$ (Table 3, 0.0-7.3 cm⁻¹) are much smaller than those obtained from similar experiments on Pt and PtAg catalysts and low-index Pt single crystals^{65, 114, 117} but similar to those measured on PdAu/Pd(111) single crystal surface alloys and Pt(335) single crystals.^{115, 117} These differences reflect the fact that dipole-dipole coupling requires similar vibrational frequencies,^{11, 12} which indicates that η^1 -CO*_{Pd} will only couple with other η^1 -CO*_{Pd} but not other forms of CO*. Monometallic Pd nanoparticles predominantly present η^1 -CO*_{Pd} at defect, edge and corner sites, however, Pt surfaces form η^1 -CO*_{Pt} at the majority of terrace sites.¹¹³ These terrace sites possess greater surface coordination than edge sites and thus show more significant effects of dipole-dipole coupling.

While the values of ν_0 show a complex dependence on the composition of Pd₁Au_x nanoparticles, the extent of dipole-dipole coupling (quantified by $\Delta\nu$) decreases monotonically with increase in the ratio of Au to Pd (Table 3) from 7.3 ± 0.2 cm⁻¹ monometallic Pd to 0.0 ± 0.4 cm⁻¹ on Pd₁Au₂₂₀. This trend holds also for Pd₁Au₃₇, Pd₁Au₅₀ and Pd₁Au₂₂₀ catalysts, which yield indistinguishable Pd coordination numbers (i.e., N_{Pd-Pd}, N_{Pd-Au}) from *in situ* XAS. Considering the inverse-cube dependence of dipole coupling shift values on average distances between sites,^{113, 114} this decrease provides strong evidence for an increase in the average distance between η^1 -CO*_{Pd} sites, and therefore, changes in the second coordination shell of Pd as the Au to Pd ratio increases.

3.5. Computational Evidence that H₂O₂ Forms by Heterolytic Pathways on PdAu_x

In previous sections, we characterized the means through which the formation of PdAu_x alloys affects the properties of Pd. These modifications may influence the mechanisms responsible for catalytic formation of H₂O₂ and H₂O. Therefore, we combine computational and experimental methods to determine the molecular processes that form H₂O₂ and H₂O on PdAu_x catalysts.

Lunsford and coworkers showed that negligible quantities of H¹⁸O¹⁶OH form during reactions of ¹⁸O₂ and ¹⁶O₂ with H₂

on Pd, which indicates that H₂O₂ proceeds through reduction of an OOH* intermediate and that O-O bonds cleave irreversibly.¹¹⁸ Within water, these reduction processes have been proposed to occur either through homolytic Langmuirian surface reactions that involve direct addition of H-atoms or by solvent-mediated processes involving proton-electron transfer through H₃O⁺ species. We demonstrated that OOH* and H₂O₂* formation by direct addition of the surface bound hydrogen atoms defined herein as H (note, # and * indicate that the OH_x intermediates and H species bind to separate sites as discussed in section 3.6) to dioxygen intermediates on Pd(111) present energy barriers 14 and 19 kJ mol⁻¹ higher than the analogous proton-electron transfer (PET) steps.⁷⁵ PdAu_x surfaces, however, may or may not exhibit the same preference for PET pathways to reduce oxygen.

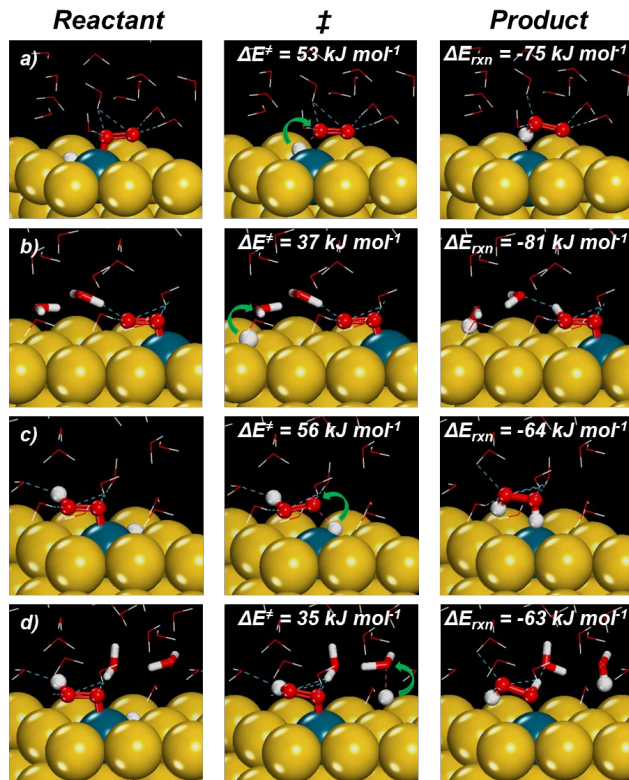


Figure 8. Reactant, transition and product state structures for (a, b) OOH* and (c, d) H₂O₂* formation by (a, c) direct surface H# transfer and (b, d) H₂O-mediated proton electron transfer on an isolated Pd monomer surface (Figure 2f).

Figure 8 shows intrinsic barriers (ΔE^\ddagger) and reaction energies (ΔE_{rxn}) and optimized structures for OOH* and H₂O₂* formation by homolytic (Figures 8a and 8c) and heterolytic (Figures 8b and 8d) processes on isolated Pd monomers in the Au(111) surface. Proton-electron transfer pathways that involve multiple explicit water molecules (i.e., a Grothuss-type mechanism) such as those shown in Figures 8b and 8d report lower intrinsic activation energies (ΔE^\ddagger) for OOH* and H₂O₂* formation than those carried out by local H# addition such as those shown in Figures 8a and 8c, by 16 and 21 kJ mol⁻¹, respectively. These differences in ΔE^\ddagger agree with similar differences calculated on Pd(111)⁷⁵ and indicate that product formation on both PdAu_x (presenting

either monomeric or oligomeric Pd atoms) and Pd catalysts occurs through similar heterolytic, solvent-mediated mechanisms.

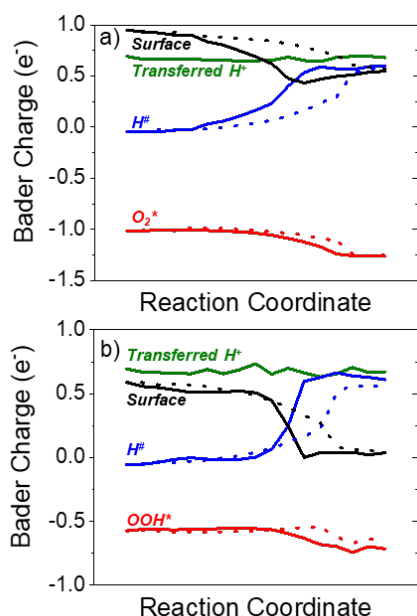


Figure 9. Bader charge profiles of O_2^* or OOH^* (—), $H^\#$ (—), the H-atom being transferred (—) and the metal surface (—) during (a) O_2^* reduction to OOH^* and (b) OOH^* reduction to $H_2O_2^*$ via a heterolytic PET type mechanism (solid lines) and via homolytic hydrogen transfer type mechanism (dashed lines). Calculations performed on an open Pd trimer surface (Figure 2b) in aqueous media.

Bader charge analysis of the surface species and the metal surface at multiple positions along the reaction coordinate provides further evidence that oxygen reduction involves heterolytic processes involving charged intermediates. Figure 9 shows the charge distribution between the different species for the OOH^* and $H_2O_2^*$ formation reactions through proton-electron transfer (solid lines) and homolytic surface reactions (dotted lines). In the PET mechanism, a surface $H^\#$ -atom oxidizes heterolytically and forms a proton that transfers to liquid water and an electron that is transferred to the metal and donated or shared with the bound O_2^* or OOH^* intermediate. Subsequently, the hydronium intermediate that forms during proton addition transfers one of its protons, to O_2^* or OOH^* . The charge on this protic hydrogen remains constant at $0.7 e^-$ during the transfer reaction. Near the completion of each reaction, the charge on O_2^* or OOH^* decreases slightly due to proton transfer from H_3O^+ . Both heterolytic and homolytic pathways display identical charge distribution for the reactive species at the reactant and product states, however, the nature of the H-atoms in the transition state differs. The positive charge carried by the protic H-atoms of water leads to barriers for PET that are consistently lower than those for direct $H^\#$ -atom transfer. In direct $H^\#$ -atom transfer, the $H^\#$ -atom transferred develops a positive charge gradually and only becomes protic after its complete addition to O_2^* or OOH^* .

3.6. Effects of H_2 and O_2 Pressures on Steady-State H_2O_2 and H_2O Formation Rates and Interpretation

Figures 10 and 11 show turnover rates for H_2O_2 and H_2O formation as functions of H_2 (Figure 10a and 11a; 20–400 kPa H_2 , 60 kPa O_2) and O_2 pressure (Figure 10b and 11b, 20–400 kPa O_2 , 55 kPa H_2) for monometallic Pd, Pd_1Au_3 , and Pd_1Au_{220} catalysts in deionized water. Rates of H_2O_2 formation increase linearly with H_2 pressure ($r_{H_2O_2} \sim [H_2]^1$) at lower values (< 100 kPa H_2) and become constant ($r_{H_2O_2} \sim [H_2]^0$) at higher values (> 150 kPa H_2) (Figure 10a). Turnover rates for H_2O formation (Figure 11a) also increase linearly with H_2 pressure at low values of $[H_2]$ (< 100 kPa) but do not change significantly at higher values (> 150 kPa). Formation rates for H_2O_2 and H_2O do not depend on O_2 pressure ($r \sim [O_2]^0$) across the wide range of conditions examined (Figures 10b and 11b), which suggests oxygen-derived species saturate active sites that form both products. Further, on both monometallic Pd^{86} and alloyed Pd_1Au_{220} (Figure S8.1), protic solvents are required to form H_2O_2 , because turnover rates are immeasurably small in aprotic solvents, such as dimethyl sulfoxide and acetonitrile. The requirement for protic solvents and the dependence of rates on reactant pressures agree with our previous reports on Pd and Pd-based bimetallic catalysts.^{41, 65, 66, 75, 86} These experimental findings agree with the conclusions from comparisons between *ab initio* calculations for heterolytic and homolytic pathways (Figs. 8) and provide further evidence that H_2O_2 and H_2O form through similar proton-electron transfer pathways and reactive intermediates on Pd and also Pd_1Au_x catalysts.

Scheme 1 shows a system of elementary steps that form H_2O_2 and H_2O by kinetically relevant proton-electron transfer steps and which reproduces the dependence of rates on H_2 and O_2 pressures. This scheme considers two types of sites ($*$ and $\#$) that account for the preference of oxygenated intermediates and $H^\#$ -atoms to bind at distinct positions on close-packed surfaces ($*$ sites bind oxygenates, and $\#$ sites bind $H^\#$ -atoms). Similar two-site kinetic models accurately describe measured power laws in ethylene hydrogenation, where $C_2H_5^*$ and $H^\#$ species do not competitively adsorb on Pt catalysts, as indicated by kinetic regimes in which rates are uninhibited by exceptionally high H_2 pressures.¹¹⁹ These two-site kinetic models may be further justified by differences in the preferred binding sites of H-atoms and oxygenates on Pd surfaces calculated by DFT^{58, 75, 106} and are rationalized in terms of the differing steric and electronic properties of the two ‘classes’ of adsorbates. Alternatively, the ethylene hydrogenation rates (and also the results in Figs. 10 and 11) may be explained by realizing that intrinsic rate constants depend on the coverages of adsorbates.¹²⁰ Here, we elect to use a two-site model that captures the known site preferences of the relevant intermediates and which provides the minimum level of complexity needed to describe measured H_2O_2 and H_2O turnover rates.

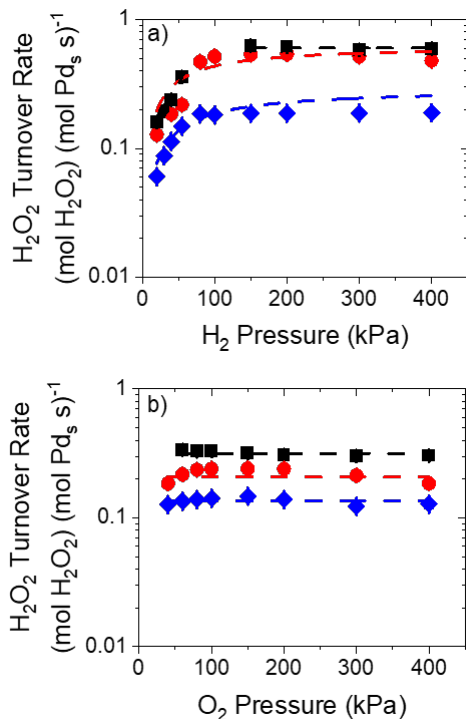


Figure 10. Turnover rates for H₂O₂ formation for monometallic Pd (■, 276 K), Pd₁Au₃ (●, 276 K) and Pd₁Au₂₂₀ (◆, 291 K) as a function of (a) H₂ pressure (60 kPa O₂) and (b) O₂ pressure (55 kPa H₂). Dashed lines indicate fits to equation 7 and 8 for H₂O₂ and H₂O formation, respectively. Rates for Pd₁Au₂₂₀ were measured at a higher temperature because H₂O formation rates are immeasurably small for this catalyst at 276 K (Figure S4.3).

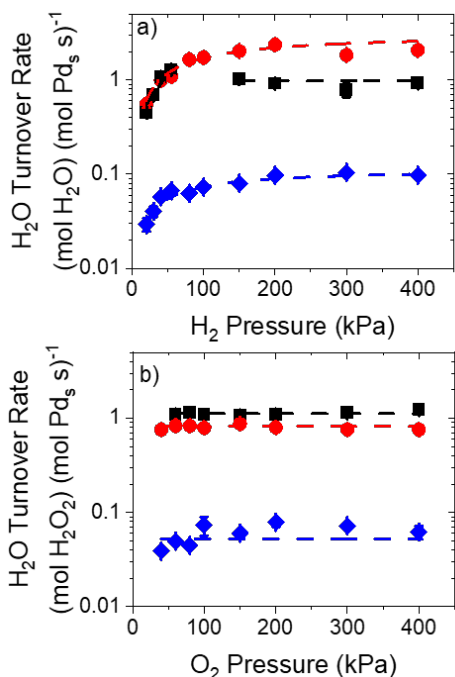
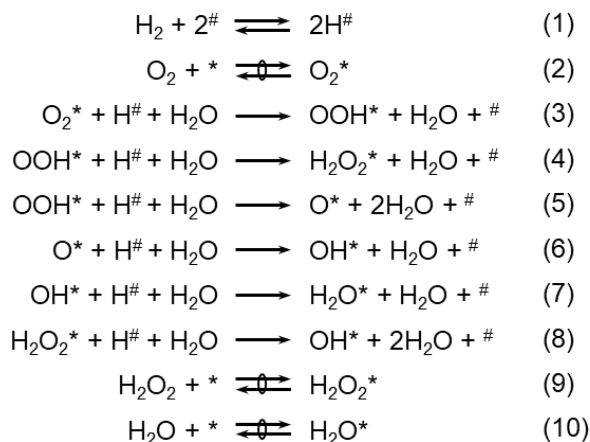


Figure 11. Turnover rates for H₂O formation for monometallic Pd (■, 276 K), Pd₁Au₃ (●, 276 K) and Pd₁Au₂₂₀ (◆, 291 K) as a function of (a) H₂ pressure (60 kPa O₂) and (b) O₂ pressure (55 kPa H₂). Dashed lines indicate fits to equation 7 and 8 for H₂O₂ and H₂O formation, respectively. Rates for

Pd₁Au₂₂₀ were measured at a higher temperature because H₂O formation rates are immeasurably small for this catalyst at 276 K (Figure S4.3).

The formation of H₂O₂ and H₂O involves dissociative adsorption of H₂ (step 1) onto unoccupied #sites to form chemisorbed H[#]-atoms. Simultaneously, O₂ adsorbs in a quasi-equilibrated manner to form O₂^{*} (step 2), which then undergoes irreversible proton-electron transfer involving H[#]-atoms and liquid-phase H₂O to form OOH^{*} (step 3). Subsequently, OOH^{*} reduces further by a second proton-electron transfer event to form either H₂O₂^{*} when the O-O bond persists (step 4) or H₂O and O^{*} when the O-O bond cleaves (step 5). Notably, O-O bonds rupture irreversibly and hence the O^{*} species must form H₂O.^{41, 65, 66, 75, 86} This process occurs by sequential proton-electron transfer events that form OH^{*} (step 6) and ultimately H₂O^{*} (step 7). Adsorbed H₂O₂^{*} and H₂O^{*} undergo quasi-equilibrated desorption to yield detectable products (steps 9 and 10, respectively).



Scheme 1. Proposed system of elementary steps describing H₂O₂ and H₂O formation on Pd and Pd₁Au_x nanoparticles. The symbol \longrightarrow denotes an irreversible reaction, whereas \rightleftharpoons signifies a reversible reaction and \rightleftharpoons corresponds to a quasi-equilibrated reaction.

Scheme 1 proposes that both H₂O₂ and H₂O form by irreversible reactions that involve H₂O-assisted reduction of oxygenates by H[#]-atoms. These reactions occur in series following a common kinetically relevant step: the reduction of O₂^{*} to OOH^{*} (step 3). Consequently, the rate of O₂ consumption follows the relationships:

$$-r_{\text{O}_2} = r_3 = \frac{r_{\text{H}_2\text{O}}}{2} + r_{\text{H}_2\text{O}_2} \quad (3)$$

where the individual product formation rates are:

$$r_{\text{H}_2\text{O}_2} = \frac{k_4}{k_4 + k_5} r_3 \quad (4)$$

and

$$r_{\text{H}_2\text{O}} = 2 \frac{k_5}{k_4 + k_5} r_3 \quad (5)$$

$$k_{app, H_2O_2} = \frac{k_1 k_4}{k_4 + 2k_5} \quad (9)$$

Within this system, the rate of step 3 is given by:

$$r_3 = k_3 [O_2^*] [H^\#] [H_2O] \quad (6)$$

where k_3 is the intrinsic rate constant for step 3, $[H_2O]$ is the concentration of H_2O (55 M) and $[O_2^*]$ and $[H^\#]$ correspond to the numbers of O_2^* and $H^\#$ surface intermediates. Equation 6 can be restated as a function of reactant pressures and intrinsic rate constants by applying the pseudo-steady state hypothesis to the coverages of reactive intermediates (OOH^* , O^* , OH^* , $H^\#$) and invoking a site balance for each type of active site. The complete forms of the resulting rate expressions and the associated derivations are shown within the Supporting Information Section S8.

These complex equations simplify in the limit of high $[O_2]$ to $[H_2]$ ratios where $\#$ -sites remain unoccupied and H_2 activates irreversibly ($r_1 \gg r_{-1}$) to yield the forms:

$$\frac{r_{H_2O_2}}{[L]} = \frac{k_{app, H_2O_2} [H_2]}{1 + K_{app} [H_2]} \quad (7)$$

and

$$\frac{r_{H_2O}}{[L]} = \frac{k_{app, H_2O} [H_2]}{1 + K_{app} [H_2]} \quad (8)$$

where the apparent rate constant for H_2O_2 formation appears as:

and the apparent rate constant for H_2O formation is:

$$k_{app, H_2O} = \frac{2k_1 k_5}{k_4 + 2k_5} \quad (10)$$

The form of the apparent adsorption constant contains numerous rate constants:

$$K_{app} = \frac{k_1 \left(\frac{k_4 + k_5}{k_4 + 2k_5} \right) \left(1 + \frac{k_2}{k_4 + k_5} + \frac{k_5 k_3}{(k_4 + k_5) \left(\frac{1}{k_6} + \frac{1}{k_7} \right)} \right)}{k_3 [H_2O]} \quad (11)$$

where k_i corresponds to the intrinsic rate constant for reaction i in Scheme 1 and $[L]$ represents the number of active sites. Equations 7 and 8 predict that rates will increase linearly with H_2 pressure at low H_2 pressure and become independent of H_2 pressure at higher H_2 pressures, and maintain constant values with changes in O_2 pressure. These predictions adequately describe H_2O_2 and H_2O formation rates on $Pd_{1}Au_x$ catalysts (Figures 10 and 11), and observations from previous reports,⁸ where at low H_2 pressures rates monotonically increase before approaching constant values at higher H_2 pressures. The differences between the apparent dependence of rates on $[H_2]$ in the two limits reflects a change in most abundant reactive intermediate (MARI) from unoccupied $\#$ sites to $H^\#$. Rates do not depend on $[O_2]$, because $\#$ sites remain nearly

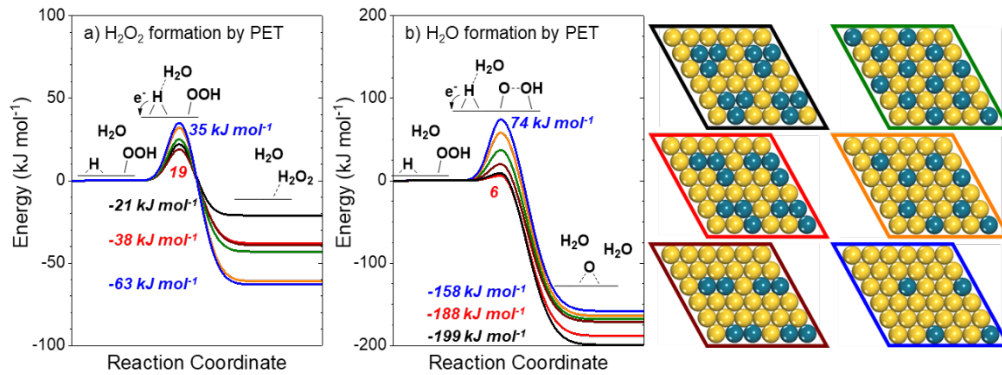


Figure 12. DFT-calculated reaction coordinate diagrams for (a) H_2O_2 and (b) H_2O formation over closed triangular Pd trimers (—), open Pd trimers (—), dimers (—), paired monomers with six Pd next-nearest neighbors (NNN=6, —), paired Pd monomers with three Pd next-nearest neighbors (NNN=3, —) and isolated Pd monomers with exclusively Au atoms at nearest and next-nearest neighbor positions (NNN = 0, —) in Au surfaces. Insets show structures for reactant, transition and product states.

saturated by a mixture of O_2^* , O^* , OH^* , and OOH^* at all conditions examined here. The rate expressions in equations 7 and 8 capture all measurements obtained on $PdAu_x$ materials but do not fully agree with rates measured on monometallic Pd nanoparticles. These discrepancies relate to a discontinuity in measured turnover rates on Pd most clearly observed in Figure 11a (H_2O formation rates drop sharply

between 55 kPa and 150 kPa H_2). This discontinuity in rates and selectivities on Pd correlates with a phase transition between metallic Pd to β - PdH_x that appears clearly in the analysis of *in situ* EXAFS.^{74, 75} Unsurprisingly, comparatively simple rate expressions (e.g., equations 7 and 8) cannot account for such phase transitions and the associated differences in rate constants. *In situ* EXAFS shows that Pd atoms

remain metallic in all Pd and PdAu_x catalysts under conditions where rates increase linearly with H₂ pressure (Figure 5; 55 kPa H₂, 60 kPa O₂). Consequently, the suppression of β-PdH_x formation cannot explain high H₂O₂ selectivities on PdAu_x catalysts shown in Figure 3 (e.g., 19 ± 1% for Pd, 95 ± 3% for Pd₁Au₂₂₀).

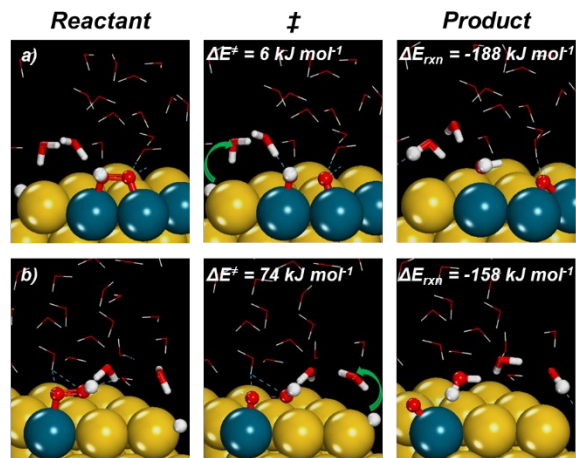


Figure 13. Reactant, transition and product states for H₂O formation by solvent-mediated proton-electron transfer (i.e., OOH* + H[‡] + H₂O → 2H₂O + O* + #) on (a) open Pd trimers and (b) isolated Pd monomers in PdAu_x surfaces.

3.7. Effects of Pd Dilution by Au on Energy Barriers for H₂O₂ and H₂O Formation

The dilution of Pd by Au does not change the mechanism by which H₂O₂ and H₂O form, and comparisons of H₂O₂ selectivities over metallic Pd and PdAu_x exclude prior hypotheses regarding the formation of the β-PdH_x phase. Therefore, the dependence of rates and selectivities on the Au to Pd ratio likely stems from differences in the intrinsic activation barriers for H₂O₂ and H₂O formation.

Table 4 shows calculated energy barriers and reaction energies for OOH* formation from O₂* and H[‡] (i.e., O₂* + H[‡] + H₂O → OOH* + # + H₂O) on each PdAu_x surface. As the number of Pd atoms involved in the three-fold hollow adsorption ensemble for H[‡] decreases from three to one, the reaction becomes more exothermic by 47 kJ mol⁻¹. Diluting Pd further destabilizes H[‡], leading to an additional 11 kJ mol⁻¹ released by the reaction. However, dilution of Pd by Au leads to an increase in the intrinsic barrier from 24 to 37 kJ mol⁻¹ across the series of surfaces. The increased barriers reflects greater difficulty for the heterolytic oxidation of H[‡] into a proton-electron pair as the reaction ensemble includes more Au atoms which increases the number of electrons in the metal, lowers the electron affinity (i.e. the work function) of the metal and inhibits electron transfer.¹²¹

Figure 12a shows calculated energy diagrams for OOH* reduction to form H₂O₂ through solvent-mediated proton-electron transfer (i.e., OOH* + H[‡] + H₂O → H₂O₂* + # + H₂O) on each PdAu_x(111) surface. Similar to OOH* formation, increasing isolation of Pd causes ΔE_{rxn} to decrease (become more negative) and ΔE[‡] to increase for the H₂O₂ formation reaction as seen in Figure 12a. The reaction becomes more exothermic due to destabilizing H[‡] by including Au in the adsorption ensemble. Intrinsic barriers increase from 19 to 35 kJ mol⁻¹, reflecting differences in electron affinities and work functions between Pd and Au. In the transition state (Figure 8d) for this reaction, on all PdAu_x surfaces, OOH* is

adsorbed in a η¹ configuration on Pd and only weakly senses neighboring atoms because it is not formally bound to them.

Table 4. Reaction energies and intrinsic activation barriers for H₂O mediated hydrogenation of O₂* to form OOH* (O₂* + H[‡] + H₂O → H₂O + # + OOH*)

Surface	ΔE _{rxn} (kJ mol ⁻¹)	ΔE [‡] (kJ mol ⁻¹)
Closed Pd trimer ^a	-23	24
Open Pd trimer ^b	-22	27
Pd dimer	-55	30
Paired Pd monomer (NNN=6) ^c	-70	34
Paired Pd monomer (NNN=3) ^d	-75	39
Isolated Pd monomer (NNN = 0) ^e	-81	37

^aClosed equilateral triangular ensemble of Pd atoms in Au (Figure 2a), ^bOpen triangular ensemble of three contiguous Pd atoms in Au (Figure 2b) ^cSurface with six Pd next-nearest neighbors (Figure 2d) ^dSurface with three Pd next-nearest neighbors (Figure 2e), ^ePd atoms with no Pd nearest or next-nearest neighbors (Figure 2f)

In Scheme 1, primary H₂O₂ selectivity is determined by competing reactions which reduce OOH* to H₂O₂ or H₂O. Figure 12b shows the energetics of H₂O formation by cleaving OOH* through solvent-mediated proton-electron transfer (i.e., OOH* + H[‡] + H₂O → O* + # + 2H₂O) on each surface. The O* species reduces further to H₂O through subsequent proton-electron transfer events (Scheme 1). Unlike OOH* and H₂O₂ formation, ΔE_{rxn} increases as Pd is isolated from -199 kJ mol⁻¹ on the closed Pd trimer surface to -158 kJ mol⁻¹ on the Pd isolated monomer surface. This results from the weaker binding of O* on ensembles containing more Au atoms to which the product binds. The intrinsic barrier for this reaction increases from 6 to 74 kJ mol⁻¹ as Pd is isolated by Au, a significantly larger change than we observed for OOH* and H₂O₂ formation. Figure 13 shows the reactant, product and transition state structures for H₂O formation on both the open Pd trimer and isolated monomer surfaces. In this reaction, the O-OH bond ruptures after electron transfer to form the O-OH⁽⁻⁾ transition state, which then accepts a proton from H₃O⁺ to make H₂O. This transition state involves multiple surface atoms required to adsorb O* and OH⁽⁻⁾* after O-O bond scission and is as such more sensitive to the surface metal coordination because both O* and OH⁽⁻⁾* bind much more weakly on more Au-rich ensembles. Thus, increasing the isolation of Pd allows us to selectively destabilize this H₂O transition state, which involves multiple surface atoms, relative to the H₂O₂ formation transition state, which only binds to one surface atom, thus increasing the H₂O₂ selectivity.

Figure 14 shows the apparent activation enthalpies for H₂O₂ and H₂O (ΔH[‡]_{H₂O₂} and ΔH[‡]_{H₂O}, respectively) formation (55 kPa H₂, 60 kPa O₂, 276-306K). These measurements were

obtained at conditions where rates of H_2O_2 and H_2O formation increase linearly with H_2 pressure, which signifies that coverages of $\text{H}^\#$ -species are insignificant. Then, the rate expressions for H_2O_2 and H_2O formation (equations 7 and 8) collapse to simpler forms:

$$\frac{r_{\text{H}_2\text{O}_2}}{[\text{L}]} = \frac{k_1 k_4 [\text{H}_2]}{k_4 + 2k_5} \quad (12)$$

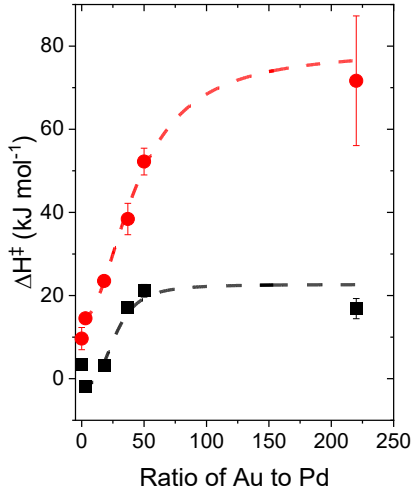


Figure 14. Change in apparent activation enthalpies for H_2O_2 (■) and H_2O (●) formation with Pd and PdAu catalyst metal content (55 kPa H_2 , 60 kPa O_2 , 276-306K)

and

$$\frac{r_{\text{H}_2\text{O}}}{[\text{L}]} = \frac{2k_1 k_5 [\text{H}_2]}{k_4 + 2k_5} \quad (13)$$

These expressions show that rates for H_2O_2 and H_2O formation depend only on $[\text{H}_2]$ and rates constants for steps 1, 4 and 5, because these elementary steps determine the coverage of the reactive OOH^* intermediate and the rates at which this species reacts to form each product. By extension, $\Delta H^\ddagger_{\text{H}_2\text{O}_2}$ and $\Delta H^\ddagger_{\text{H}_2\text{O}}$ are functions of the intrinsic activation enthalpies for H_2 activation, OOH^* reduction to H_2O_2 and OOH^* reduction to H_2O . However, the complex forms of equations 12 and 13 prevent precise molecular interpretations of experimental values for $\Delta H^\ddagger_{\text{H}_2\text{O}_2}$ and $\Delta H^\ddagger_{\text{H}_2\text{O}}$.

Despite these complications, the rate expressions, and therefore the definitions of apparent activation enthalpy, remain constant across all catalysts examined in this study, so $\Delta H^\ddagger_{\text{H}_2\text{O}_2}$ and $\Delta H^\ddagger_{\text{H}_2\text{O}}$ may be compared to one another in a physically meaningful way. Values of $\Delta H^\ddagger_{\text{H}_2\text{O}}$ increase as a strong function of Au to Pd ratio from Pd ($8 \pm 4 \text{ kJ mol}^{-1}$) to $\text{Pd}_1\text{Au}_{220}$ ($68 \pm 4 \text{ kJ mol}^{-1}$), yet $\Delta H^\ddagger_{\text{H}_2\text{O}_2}$ values increase by only 15 kJ mol^{-1} . Notably, $\Delta H^\ddagger_{\text{H}_2\text{O}}$ values increase monotonically while $\Delta H^\ddagger_{\text{H}_2\text{O}_2}$ initially increase with the Au to Pd ratio but then approach constant values for Au to Pd ratios of 37 to 220. These comparisons demonstrate that the high H_2O_2 selectivities observed on PdAu_x materials (Figure 3) reflect the preferential destabilization of transition states that cleave the O-O bond within OOH^* intermediate, which agrees with the results from DFT calculations on repre-

sentative surfaces (Figure 12). The monometallic Pd catalyst exhibits low ΔH^\ddagger values ($<15 \text{ kJ mol}^{-1}$) for both reactions, consistent with previous reports from our group.^{65, 66, 75, 86} The Pd_1Au_3 catalyst exhibits similar selectivities and ΔH^\ddagger values to the monometallic Pd catalyst for both reactions. Characterization results from FTIR of adsorbed CO and *in situ* EXAFS show significant amounts of Pd-Pd surface coordination in this catalyst, indicating the increases in ΔH^\ddagger values, and therefore selectivity, result from an absence of Pd-Pd surface coordination.

While differences in $\Delta H^\ddagger_{\text{H}_2\text{O}_2}$ and $\Delta H^\ddagger_{\text{H}_2\text{O}}$ values between catalysts cannot be precisely attributed to intrinsic barriers specific steps in Scheme 1, the difference between $\Delta H^\ddagger_{\text{H}_2\text{O}_2}$ and $\Delta H^\ddagger_{\text{H}_2\text{O}}$ can be (Supporting Information Section S8.3), as the rate ratio of H_2O_2 to H_2O formation takes the form:

$$\frac{r_{\text{H}_2\text{O}_2}}{r_{\text{H}_2\text{O}}} = \frac{k_4}{2k_5} \quad (14)$$

which implies that the difference ($\Delta\Delta H^\ddagger$) between the experimentally measured apparent barriers $\Delta H^\ddagger_{\text{H}_2\text{O}_2}$ and $\Delta H^\ddagger_{\text{H}_2\text{O}}$ is equal to the difference between intrinsic barriers ΔH^\ddagger_4 and ΔH^\ddagger_5 . $\Delta\Delta H^\ddagger$ represents the difference between the stability of the transition states for steps 4 and 5 (Scheme 1), because both H_2O_2 and H_2O form by reactions among the same intermediates ($\text{H}^\#$, OOH^* , and H_2O). Importantly, experimentally measured $\Delta\Delta H^\ddagger$ values may be directly compared to differences in intrinsic barriers calculated by DFT and do not require the assumptions made in Section 3.4 to simplify equations 7 and 8.

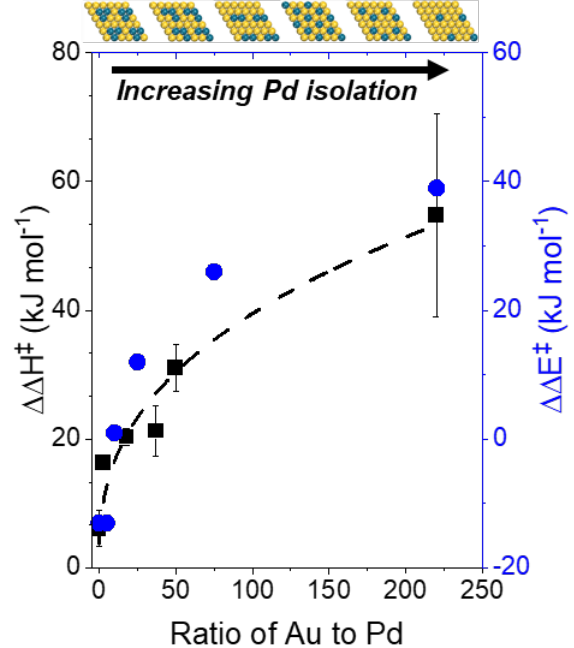


Figure 15. Differences between apparent activation enthalpies for H_2O_2 and H_2O formation ($\Delta\Delta H^\ddagger = \Delta H^\ddagger_{\text{H}_2\text{O}} - \Delta H^\ddagger_{\text{H}_2\text{O}_2}$) measured experimentally (■) as a function of the Au to Pd ratio obtained on PdAu_x catalysts (55 kPa H_2 , 60 kPa O_2 , 276-306 K), and calculated differences between the intrinsic activation energies for step 5 and step 4 ($\Delta\Delta E^\ddagger =$

$\Delta E^\ddagger_5 - \Delta E^\ddagger_4$, Scheme 1) obtained from DFT calculations (●) carried out on representative $\text{PdAu}_x(111)$ surfaces.

Figure 15 shows the differences between the intrinsic barriers for steps 4 and 5 obtained by both theory and experiment for multiple PdAu_x surfaces. In both cases, the difference in apparent barriers increases with the Au content of PdAu_x , indicating an increasing enthalpic preference for the H_2O_2 transition state over the H_2O transition state. Thus, PdAu_x surfaces which are more dilute in Pd show higher H_2O_2 selectivities; this trend continues past the point where all of the Pd exists as Pd monomers, showing that the second coordinative shell of Pd can have an effect on catalysis. This effect may arise from potentially different electronic structures of Pd in each PdAu_x alloy or from geometric differences between surfaces.

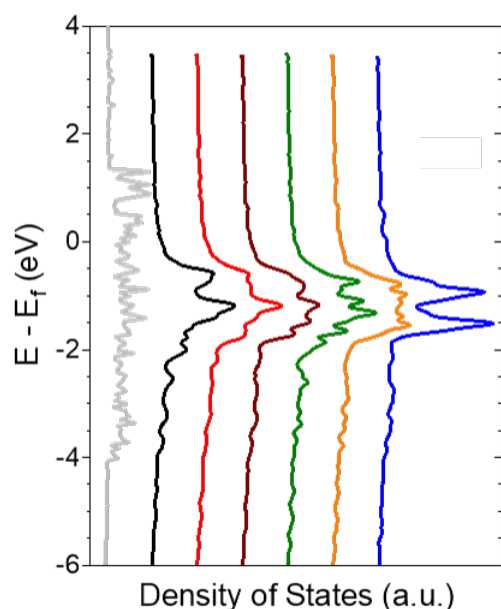


Figure 16. Projected density of states for Pd(111) (—) and the closed triangular Pd trimer (—), open Pd trimer (—), dimer (—), paired monomer (NNN=6) (—), paired monomer (NNN=3) (—) and isolated monomer (—) in Au surfaces.

To distinguish these two possible explanations, we show the projected density of states (DOS) for each PdAu_x surface in Figure 16 and compare to Pd. The d -band center for Pd atoms in PdAu_x surfaces shows small and nonsystematic changes from closed and open Pd trimers (-1.511 eV and -1.514 eV, respectively) to dimers (-1.538 eV), paired monomers (-1.527, NNN = 6; -1.550 eV, NNN = 3) and isolated monomers (-1.580 eV). In contrast, the d -band center for Pd(111) is -1.714 eV.⁷⁵ The d -band structure for all PdAu_x surfaces is narrow (fwhm ~ 1 eV), unlike Pd(111) (fwhm ~ 2.5 eV). These calculations suggest that the narrow, free-atom-like d -band structures calculated by Thirumalai and Kitchin for Pd, Pt, Ir, Rh and Ni single-atoms in Au, Cu, and

Ag⁵³ and measured by Greiner et al., for Cu single-atoms in Ag⁵⁴ are properties of dilute alloys and not only single-atom alloys: the narrow d -band structure emerges before reaching the single atom limit. These electronic comparisons show that the dilution of Pd by Au causes changes both in the surface electronic and geometric structure, which affect rate and equilibrium constants for the elementary steps described in Scheme 1. The electronic and geometric contributions, therefore, cannot be fully decoupled for any catalyst. The differences between the positions of the d -band centers of the PdAu_x surfaces shift minimally among the trimer and monomer structures (Figure 16), however, these surfaces clearly expose geometrically distinct ensembles of Pd atoms. Consequently, the changes in geometric structure correlate more strongly with differences in H_2O_2 selectivity and activation barriers, which indicates that coordination of Pd atoms within these ensembles provide the selective stabilization of transition states for H_2O_2 over those that form H_2O . As Pd atoms become increasingly isolated by Au, activation barriers for both H_2O_2 and H_2O formation increase, but transition states that cleave O-O bonds sense these differences more strongly because they exchange greater amounts of charge (i.e., form more bonds) with the surface.

4.0. Conclusions

Comparisons among steady-state rates for the formation of H_2O_2 and H_2O , analysis of *in situ* X-ray absorption spectra, examination of *ex situ* infrared spectra of CO^* -species, and quantum chemical simulations carried out on representative surfaces demonstrate that the isolation of Pd atoms within Au domains forms active sites that preferentially form H_2O_2 and exhibit selectivities that increase with the separation between monomeric Pd atoms at surfaces. Electroless deposition of Pd onto Au nanoparticles results in uniform ensembles of nanoparticles that give high selectivities towards H_2O_2 (> 60%) at Au to Pd ratios (Au:Pd > 18) that lead to materials with Pd-Pd coordination numbers nearing zero, as determined by *in situ* XAS and *ex situ* infrared spectra of chemisorbed CO. Further increases in Au to Pd ratios lead to greater selectivities that approach 100% for $\text{Pd}_1\text{Au}_{220}$. Statistical arguments and vibrational Stark effects indicate that these increases reflect the loss of next-nearest neighbor Pd atoms (i.e., second coordination shell Pd). DFT calculations show H_2O_2 and H_2O form by solvent mediated PET processes, which present lower barriers than plausible homolytic surface reaction on representative PdAu_x surfaces in water. These findings agree with steady-state rates measured as functions of reactant pressures and the requirement for protic solvents for H_2O_2 formation. The mechanism and kinetically relevant steps for H_2O_2 and H_2O formation remain consistent across Pd and PdAu_x catalysts. Measured H_2O_2 selectivities primarily depend on differences between ΔH^\ddagger for parallel reaction pathways of a common surface intermediate (OOH^*): reduction by PET to form H_2O_2 or a dissociative PET process that gives H_2O . Experimentally determined ΔH^\ddagger for both pathways increase with Au to Pd ratio but differ in their sensitivity to Pd isolation. These measured differences between ΔH^\ddagger for H_2O_2 and H_2O formation correlate strongly with DFT calculations of activation energies for the corresponding processes. These

results indicate that both nearest and next-nearest Pd atoms stabilize transition states that dissociate OOH*, however, the formation of H₂O₂ seems to only depend upon the identity of nearest neighbor atoms. The different structural sensitivities of these steps predominantly reflect the number of surface atoms required to bind the transition and product state of these pathways.

Interpretation of these findings suggest that increased selectivities of H₂O₂ on AuPd catalysts described here (and in prior reports) largely originate from resulting geometric arrangements of Pd and Au atoms within active site ensembles and not from interatomic charge transfer, suppression of PdH_x formation, or from changes in the reaction mechanism. Furthermore, measurements presented here demonstrate that careful synthesis of these dilute Pd atoms on surfaces of Au nanoparticles produces catalysts with an uncommon combination of high H₂O₂ selectivities and high stabilities in pure water. These materials represent a significant advance in the development of catalysts for the direct synthesis of H₂O₂ and suggest strategies for new catalysts compositions and structures.

ASSOCIATED CONTENT

Supporting Information. Transmission electron micrographs, X-ray absorption spectra and fits, infrared spectra of adsorbed CO*, rate equation derivations, depictions of DFT- reaction coordinates.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We gratefully acknowledge Dr. Wacław Swietch, Dr. Adam Hoffman and Prof. Simon Bare for training and assistance in data collection. This work was carried out in part in the Frederick Seitz Materials Research Laboratory Central Research Facilities, University of Illinois. We also acknowledge computational resources from the Minnesota Supercomputing Institute. TR, JSA and DWF acknowledge generous support from the National Science Foundation (CBET- 15531377), the Energy Biosciences Institute and Shell International Exploration and Production, Inc. MN acknowledges support from National Science Foundation CSOE (CHE-2002158). AMK acknowledges funding from the American Chemical Society Petroleum Research Fund award number PRF# 55575-ND5. Use of the Stanford Synchrotron Radiation Light Source (Beamline 9-3, user proposal 4938) was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515.

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